INK AND PAPER IN THE PRINTING PROCESS

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ANDRIES VOET

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1952

INTERSCIENCE PUBLISHERS
NEW YORK LONDON

Library of Congress Catalog Card Number 52-11179

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ED 655.3
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57/82

INTERSCIENCE PUBLISHERS, Inc., 250 Fifth Avenue, New York 1, N. Y.

For Great Britain and Northern Ireland:
INTERSCIENCE PUBLISHERS Ltd., 2a Southampton Row, London W. C. 1.

PRINTED IN THE UNITED STATES OF AMERICA

TO

JULIUS BEKK

Pioneer, Teacher, Friend

PREFACE

This book is intended as an introduction to the physics and chemistry of ink and its interaction with paper in the major printing processes. It is written for the more experienced graphic arts student with basic understanding of science.

Although it has been universally recognized that press performance depends primarily on the physical characteristics of the ink, in the books dealing with formulations and technology of inks as well as with the chemistry of ink raw materials little attention has generally been paid to inks as physical systems.

During the course of his lecture series at New York University it became apparent to the author that few of the scientific investigations carried out in recent years on the interaction of ink and paper are easily accessible to students. This book is intended primarily to fill their need.

Certain aspects of inks, such as color, gloss, and dispersion, which might be considered as falling within the scope of this book, have purposely been omitted because excellent reference books have been published on these subjects in the English language. They are listed below by topic:

Color: P. J. Bouma, "Physical Aspects of Color," N. V. Philips Gloeilampenfabrieken, Eindhoven, Holland, 1947; Elsevier Book Co., Houston, Texas.

Gloss: V. G. W. Harrison, "Gloss," Chemical Publishing Co., Brooklyn, 1949.

Dispersion: E. K. Fischer, "Colloidal Dispersions," John Wiley & Sons, Inc., New York, 1950.

Technology: H. J. Wolfe, "Printing and Litho Inks," 4th ed., MacNair-Dorland Co., New York, 1949.

Literature Review: Carleton Ellis, "Printing Inks," Reinhold Publishing Corporation, New York, 1940.

The author is indebted to Messrs. J. Bekk, I. M. Bernstein, and L. H. Sjodahl, and to the London School of Printing as well as to Interchemical Corporation, for their permission to reproduce some of their previously published photomicrographs in this book.

The author hopes to have shown in this book that the old art of ink making is gradually maturing into a science. The end point, however, is not yet in sight.

ANDRIES VOET

Borger, Texas
August, 1952

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PART I

INK AND PRESS

CHAPTER I

THE FUNCTION OF INK

A. INTRODUCTION

The function of a printing ink is to provide a contrast coating. While paint and lacquer films are usually protective coatings, sometimes decorative coatings, and seldom contrast coatings, ink films form primarily a contrast with the background, showing an image which brings a message to the observer. The contrast coating, therefore, must show a difference in brightness with the background in order to be visible. In addition, a difference in color will emphasize the contrast while, finally, a difference in specular reflection or gloss will make the existing differences even more pronounced upon observation at different angles.

The distinction in function between a paint and an ink film, however, does not clarify the fundamental differences. While paints are applied to the surface with a brush, a spraygun, by dipping or rarely with a roller, inks are always applied with printing machinery. The characteristics of inks are therefore determined by the fact that they have to be suitable for application by means of printing presses.

A difference in brightness between printed and unprinted parts of the surface is usually attained in black and white by producing opaque ink films which show a brightness difference with the unprinted surface. In colored inks opaqueness emphasizes the contrast. In multicolor printing, however, transparency is required in the successive ink films.

To provide a contrast it is quite satisfactory, in principle, to use a simple powdered coloring material, as is done in Xero printing, a newly developed method of printing at present in the experimental stage. This is possible in Xero printing because the problem of a proper distribution of the coloring bodies has been solved in an ingenious way, by means of static electric charges produced on the image spots of the plate, to which the pigment particles adhere. In all conventional printing processes, however, the presses are suitable

only for distributing a liquid body, making it necessary to use a liquid ink.

Few liquids are strongly colored. Inks, therefore, can be made by dissolving a powerful coloring body or dye in a solvent. More often, for reasons discussed later, insoluble coloring materials or pigments are dispersed in an extremely finely divided form in a liquid. The liquid is thus merely a color carrier or vehicle—a necessary evil, for the pigment or dye must be carried by means of the distribution mechanism of the printing press to the surface to be printed.

The need for the carrier liquid ceases to exist after the ink film has been deposited on a surface, usually paper. In fact, the liquid film on paper is now definitely undesirable, since the print will be smeared and smudged if touched or mechanically handled. The major problem in inks is really elimination of the liquid carrier, after termination of its usefulness, or changing it into a harmless, or possibly even useful, solid film. This process is arbitrarily called *drying,* although it has little, if anything, to do with the commonly accepted meaning of the word. We shall, however, use this generally accepted expression and define ink drying as the process of changing a liquid ink film into a solid composition.

B. SYSTEMS OF DRYING

A number of systems have been developed for the drying of inks, severai of which have acquired prominence in practical printing. They may generally be classified as physical or chemical methods of drying.

The physical methods of drying are the simplest. Solidification by the cooling of a hot melted composition, fundamentally the most logical process, although applied commercially, has met with so many difficulties of a secondary and often mechanical nature that, thus far, it has not been successful. This process is known as the coldset process.

A second physical method, solvent evaporation, is widely applied in a number of printing processes, such as the gravure, aniline, and heatset processes.

A third physical method, drying by absorption, is predominantly applied in newspaper printing. In this process the liquid vehicle filters into a porous paper stock, leaving the pigment on the surface.

A fourth physical method, drying by gelation, has recently become more prominent. In using this method a liquid vehicle, usually con-

sisting of a thin liquid in which a rubbery or resinous compound has been dispersed, solidifies by gelation. After the fluid part of the vehicle has been drained into the porous paper stock, gelation sets in. The transformation of the comparatively soft gel into a hardened solid usually occurs by secondary physical or chemical changes.

A fifth physical method of drying is by precipitation. In this method a fluid ink film is forced to absorb a liquid or a vapor for which it has only a limited compatibility. After the maximum tolerance has been exceeded, precipitation of a dissolved resinous binder sets in and a partly solid film is formed. Complete solidification gradually occurs later, usually by other physical methods, such as evaporation and penetration of excess liquid into the paper stock.

Of the chemical methods, the most prominent and probably the oldest and closest in nature to the drying of paints is drying by a combination of oxidation and polymerization known as oxidative polymerization. The carrier liquid is generally a drying oil, linseed oil being a prominent one. In a film of drying oil exposed to the air, chemical changes set in. The film absorbs oxygen, which is chemically bound, and this is followed by a process of polymerization, the formation of larger molecules with different physical characteristics, leading ultimately to the formation of a solid film.

Another chemical method of ink drying may be indicated by the general name "curing." In curing, a liquid resinous film may form a solid polycondensation product. Thus, a thermosetting resin can be cured by heat, a process accelerated by the addition of a catalyst. Curing has not met with marked commercial success in printing inks because the process is relatively slow.

Although other chemical methods are possible, very little, if any, practical application has been made of them. For instance, of two reacting chemicals forming a solid colored compound, one of the materials, which should be colorless, could be embedded in the paper while the other forms the ink. Equally possible is a method employing as ink a mixture of reactants which form a solid colored compound with measurable speed only in the presence of a catalyst. By using a paper in which a liquid or solid catalyst is embedded or by exposing the print to a gaseous catalyst, the reaction would proceed quickly to form the desired end product. These methods at present are only of theoretical interest, owing to the lack of a proper system of reactants

and catalysts, but, if a suitable reaction mechanism were discovered, such a method could become of great significance overnight.

From practical observation it appears that all physical methods of ink drying proceed more rapidly than chemical methods. This is mainly due to an induction period which precedes the organic reactions used thus far in film drying. This period cannot be eliminated entirely by the application of higher temperatures and by the incorporation of catalysts. It is true that many chemical reactions, such as decomposition reactions and ionic reactions, have no induction period, but up to the present they have not found any application in the printing process.

C. SYSTEMS OF PRINTING

Although the method employed in the drying system determines the main ink characteristics, the type of printing press used is also of great importance.

Basically there are three printing processes. Typography denotes printing from a raised surface. Planography is printing from a substantially flat surface in which the printing areas have physical characteristics different from those of the nonprinting areas. Finally,

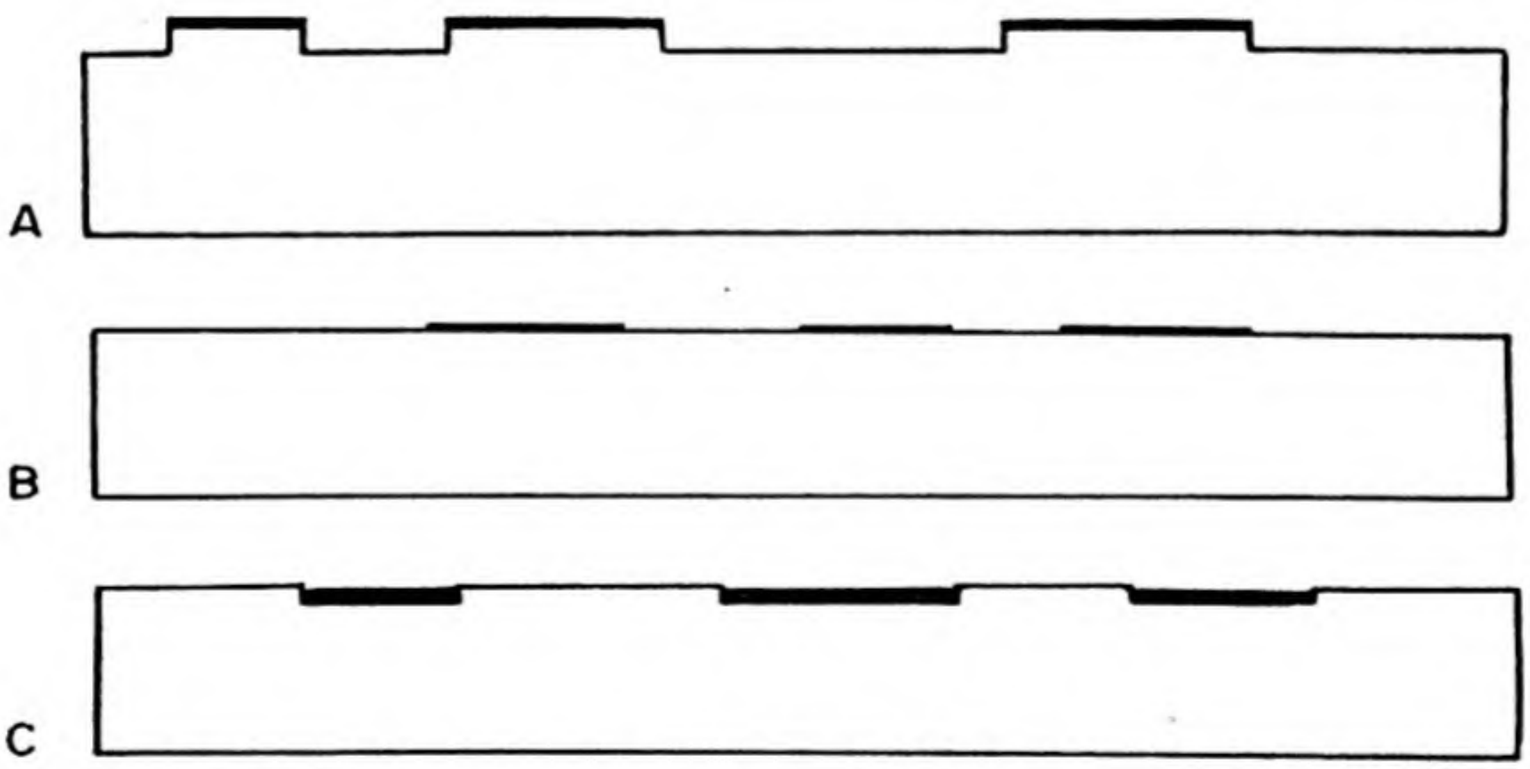


Figure I-1. Schematic representation of plates used in the main printing processes: (A) typography; (B) planography; (C) intaglio.

intaglio printing employs depressed, engraved plates. The differences are schematically indicated in Figure I–1, where A is a cross section of a typographic plate, B of a planographic plate, and C of an engraved plate. The open part indicates the plate, while the solid represents the ink. In typography the ink is deposited only on the raised parts,

and the reproduction on paper is an image of the raised parts of the plate. In intaglio printing the ink is lifted from the depressions in the plate, and the reproduction is made from the engraved image. Finally, in planography the ink is deposited only on the so-called ink-receptive areas. The physically different nonreceptive areas are usually dampened with water to prevent ink reception. Ink-receptive areas have a water-repulsive surface coating and do not accept water. The reproduction on paper, therefore, is made by the ink-receptive image areas.

Not only the printing system but also the particular type of press used will determine the most desirable characteristics of the ink. In typography, for instance, the slower platen presses have ink requirements different from the faster automatic or flatbed cylinder presses, whereas the higher speed rotary presses require rapidly distributing inks. In intaglio printing the extremely viscous inks for copper or steel engravings, usually hand-wiped, are completely different in characteristics from the very fluid rotogravure inks used in high-speed rotary intaglio printing.

The oldest form of planography, lithography proper, used a natural stone (porous Bavarian limestone consisting mainly of calcium carbonate) as the basis for the image. The same principle is applied in the modern "offset lithography," where metallic plates are used, mostly zinc or aluminum, and more recently polymetallic in nature. In offset lithography the image is transferred from plate to paper via a rubber blanket. The inks used in the slow lithography differ greatly in consistency from the modern high-speed offset inks.

The function of the ink in the major printing processes will be examined under varying conditions from a physical and chemical point of view. This study is advantageously undertaken with an initial limitation to a single aspect of ink behavior. A broadening to other applications may then generally be carried out later.

CHAPTER II

MEASUREMENT OF THE FLOW OF INKS

A. INTRODUCTION

The study of flow properties of matter is known as rheology, a branch of physics which has only recently been established as a separate science. The flow properties of ink, therefore, are advantageously analyzed on the basis of rheological methods.

One of the major problems in the manufacture of printing inks is to assure their proper distribution on the press, a process governed by the flow characteristics of the ink. In addition, accuracy in reproduction of elements, whether halftone dots or letters, determines the quality of the print. The degree of distortion during the reproduction of these elements is greatly influenced by the flow of the ink. The tackiness, or tack, of the ink, which has a profound influence upon ink transfer, is related to the rheological properties of the ink. It is therefore understandable that in the application of ink its flow is a quality of prime importance. To evaluate properly the complicated flow characteristics of an ink, the general rheological approach will be followed.

B. THE RHEOLOGICAL DIAGRAM

In a flowing liquid, layers of the fluid are caused to move in relation to one another. This motion meets with a resistance, large in viscous liquids and small in more fluid liquids, which is characteristic of the inner friction in the liquid. An orderly flow in parallel planes, with each liquid layer moving past its nearest neighbor with the same velocity, is said to be laminar. A turbulent flow is a disorganized form in which no regular parallel flow pattern exists.

Consider two layers of unit area of contact in a series of equidistant parallel layers of liquid in laminar flow which are at a distance Δr and are moving relatively to each other with a velocity ΔV. The force S required to maintain the velocity difference is, according

to a pronouncement of Newton, proportional to the difference in tangential velocity per unit of distance. Indicating the proportionality factor with η, we find:

$$S = \eta_i(\Delta V/\Delta r) \qquad (1)$$

For a continuous change in tangential velocity the difference in speed per unit distance becomes equal to the velocity gradient, also known as the rate of shear, D. Thus,

$$S = \eta(dv/dr) = \eta D \qquad (2)$$

The coefficient η, characteristic of each liquid, is known as the coefficient of viscosity. It is defined by equation (2) as the numerical value of the tangential force per unit area exerted by one layer of liquid upon another at unit distance and moving with unit velocity relative to the other layer in its own plane. It is therefore the tangential shearing force per unit area which produces a unit rate of shear.

Liquids which obey Newton's fundamental equation are known as Newtonian liquids. To find out whether or not a liquid has a Newtonian flow type a graphic representation of the flow characteristics of a liquid is made in a rheological diagram. In the graph of Figure II–1 the shearing force S is plotted against the rate of shear D produced by the force. The proportionality between S and D for the Newtonian liquid is indicated by the straight line through the origin. From equation (2) it appears that the viscosity coefficient η may be found from the diagram as the cotangent of the angle of the line with the force axis. It is expressed in poises and has the dimension $ml^{-1}t^{-1}$.

Many common liquids, such as water, ethanol, benzene, and glycerin, satisfy Newton's law. A number of liquids, however, show a more complicated flow pattern. Such systems are known as non-Newtonian liquids. An example, a different type of flow is indicated in Figure II–2. It represents a system in which a minimum force or yield value has to be applied before the system starts to flow. Once flow is produced the rate of shear attained is proportional to the excess of the stress over the yield value, f. Thus,

$$D = \mu(S - f) \qquad (3)$$

in which μ is known as the mobility, indicated in the diagram as the tangent of the straight line with the stress axis. This particular type of flow is known as ideal plastic flow. The conception of ideal plastic

flow was introduced by Bingham.[1] A material exhibiting such flow is known as an ideal plastic or a Bingham body. (The term "plastic" refers to bodies exhibiting non-Newtonian flow and is, of course, independent of chemical constitution.)

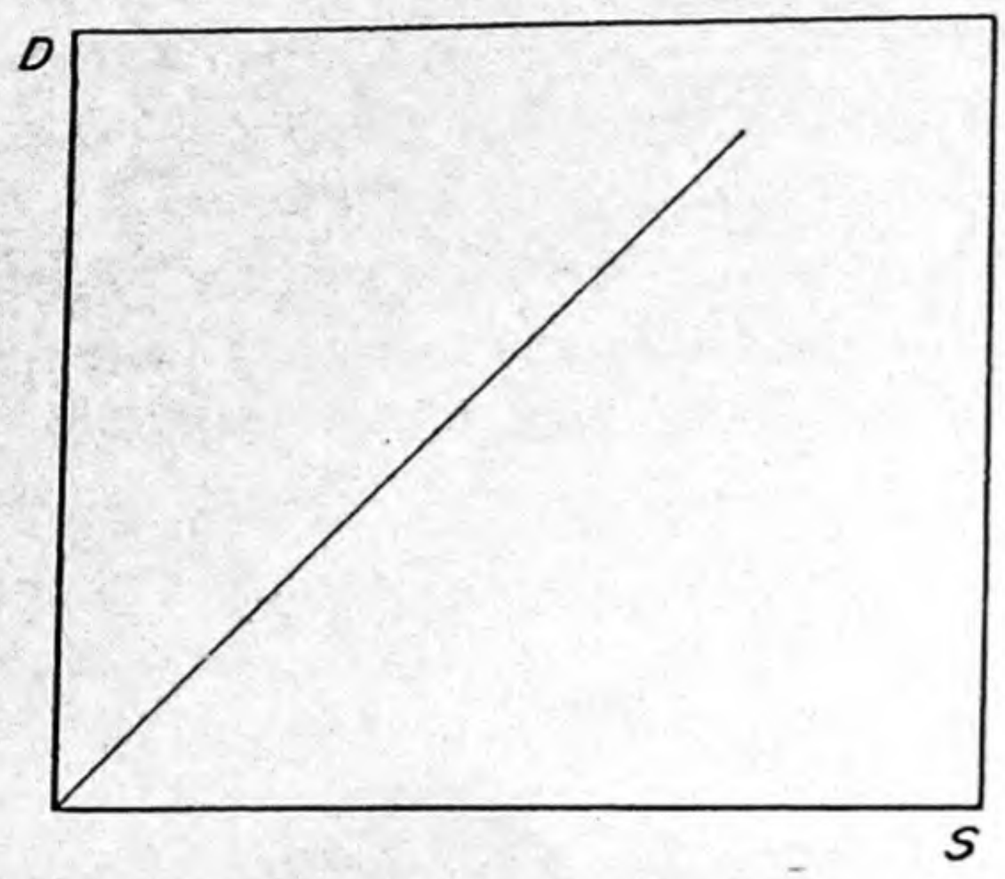


Figure II-1. Rheological diagram for a Newtonian liquid.

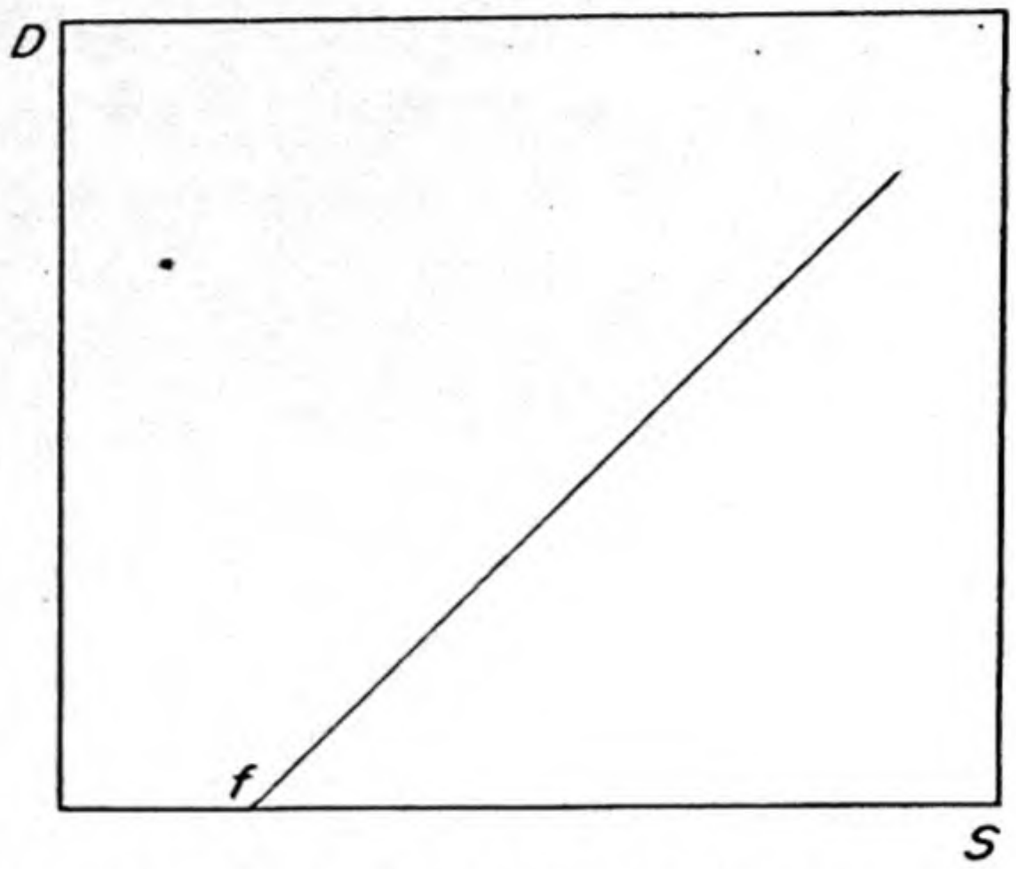


Figure II-2. Rheological diagram representing ideal plastic flow.

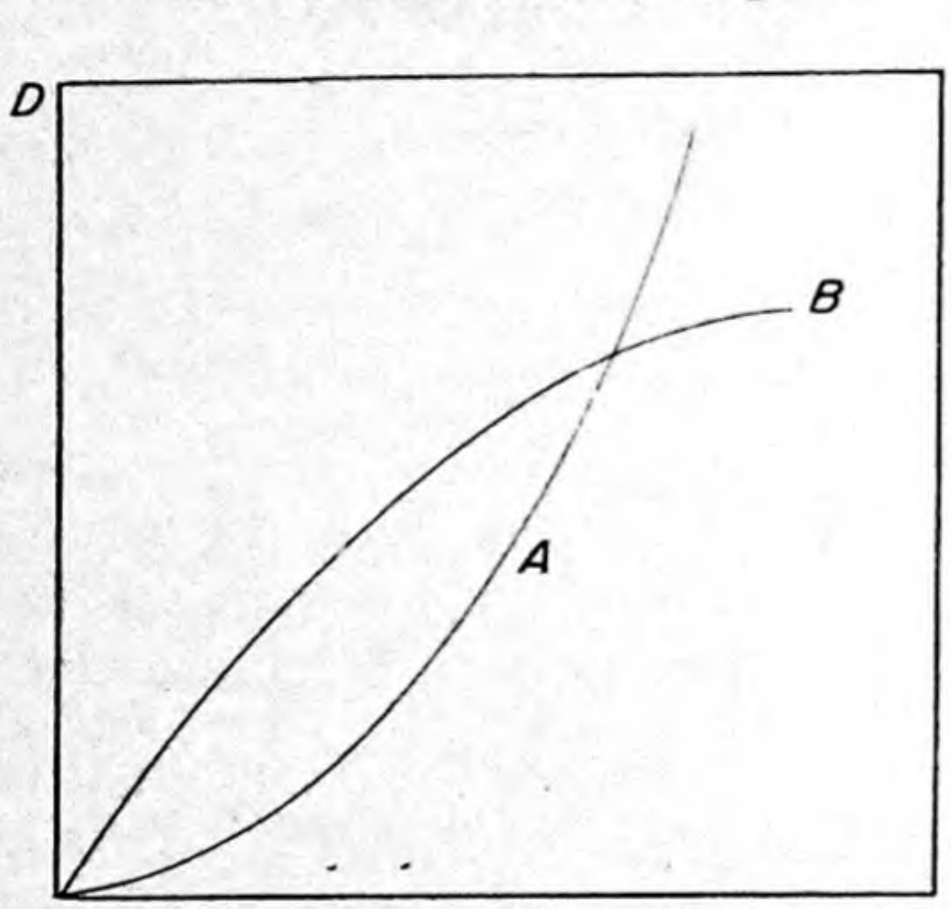


Figure II-3. Rheological diagram representing pseudoplastic (*A*) and dilatant (*B*) flow.

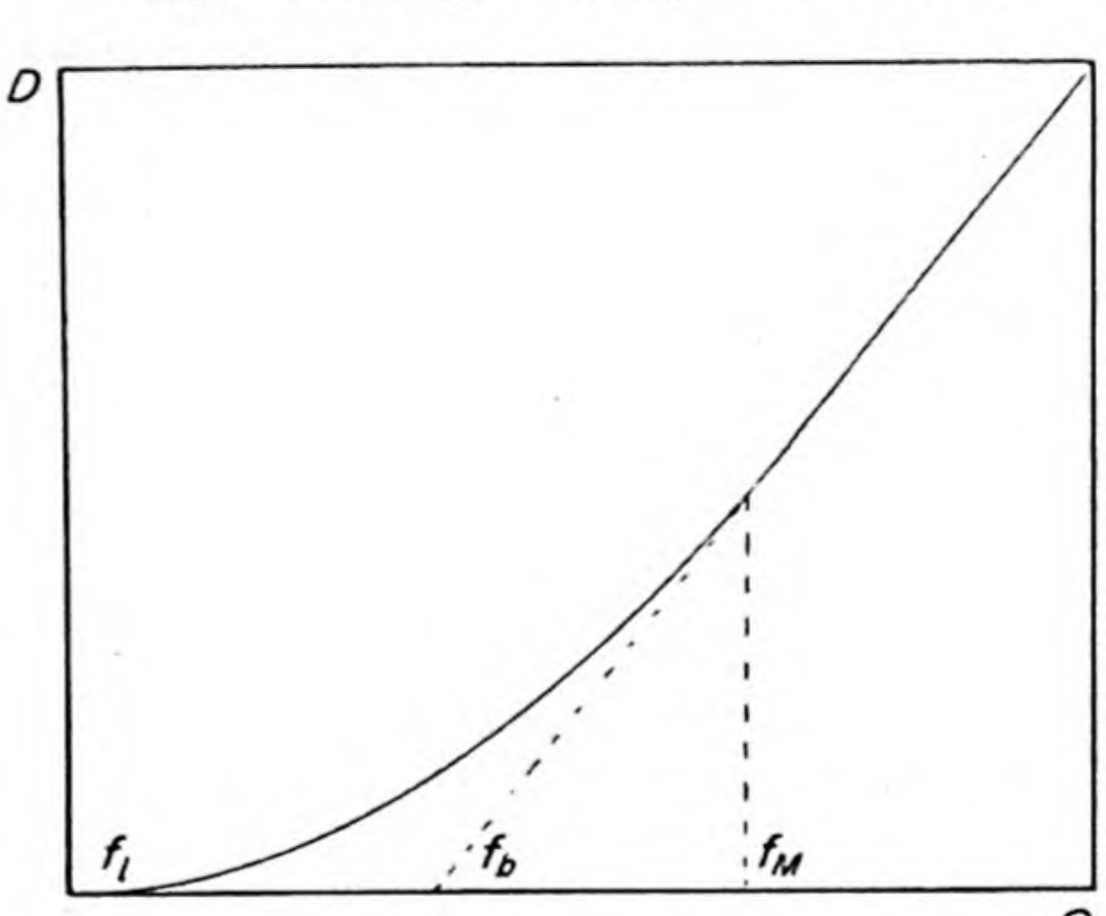


Figure II-4. Rheological diagram representing nonideal plastic flow.

Curve *A* in Figure II–3 represents another type of flow in which the rate of shear increases continuously with increased stress. Such systems are known as pseudoplastic systems. Systems in which the rate of shear decreases with increasing stress are known as dilatant.

[1] E. Bingham, *Natl. Bur. Standards (U. S.), Sci. Papers 278* (1916).

Since dilatancy is rarely observed in conventional printing inks, it is not extensively discussed here.

The curve of Figure II–4 represents nonideal plastic flow. According to Houwink[2] three types of yield values may be distinguished. The lower yield value f_l is that value of the shearing stress at which flow starts. The maximum yield value f_m is the value of the shearing stress above which the type of flow is characterized by a linear force-flow relationship. Again, f_B represents a theoretical yield value obtained by intersection of the extention of the linear part of the diagram to the stress axis. The Bingham yield value f_B represents the theoretical yield value for a Bingham body, showing ideal plastic behavior. Green and Weltmann[3] showed that the three yield values are not basically different, but are functions of the same yield value. They become apparent as a result of a nonlaminar flow pattern occurring in all viscometers at low shearing stresses in plastic liquids, as will be more fully discussed later.

C. MEASUREMENT OF VISCOSITY OF INKS

The instruments used to determine the viscosity of liquids are known as viscometers. Several types of viscometers are in existence, the most important of which are the efflux and the rotational viscometers.

The problem of the determination of the viscosity of a Newtonian liquid is relatively simple. A single reading of the flow at any given stress will allow the construction of a complete diagram of the type shown in Figure II–1. The coefficient of viscosity is found from equation (2).

Unfortunately most printing inks are plastics, often far from Newtonian, thus greatly complicating the measurement of the viscosity of inks.

1. Capillary Viscometers

The capillary viscometer is the prototype of an efflux instrument. In this type of viscometer a liquid moves under pressure through a capillary, and the time necessary for a given volume of the liquid to

[2] R. Houwink, *Elasticity, Plasticity and the Structure of Matter*, Cambridge Univ. Press, London, 1937.
[3] H. Green and R. N. Weltmann, *Ind. Eng. Chem. Anal. Ed.*, *15*, 201 (1943).

pass through the capillary is measured. The viscosity of a Newtonian liquid may then be calculated from the classical Poiseuille-Hagenbach relationship

$$\eta = \pi P r^4 / 8 l Q \tag{4}$$

in which P is the pressure, r the radius, and l the length of the capillary, while Q is the volume of liquid discharged per unit of time.

Capillary viscometers are suitable for Newtonian liquids and may be used for most solvents and oils. At moderate rates of shear Newtonian liquids show laminar flow in a capillary. At high shearing stresses, however, turbulence sets in. Reynolds[4] showed that the type of flow in a capillary is determined by the velocity V of the liquid,

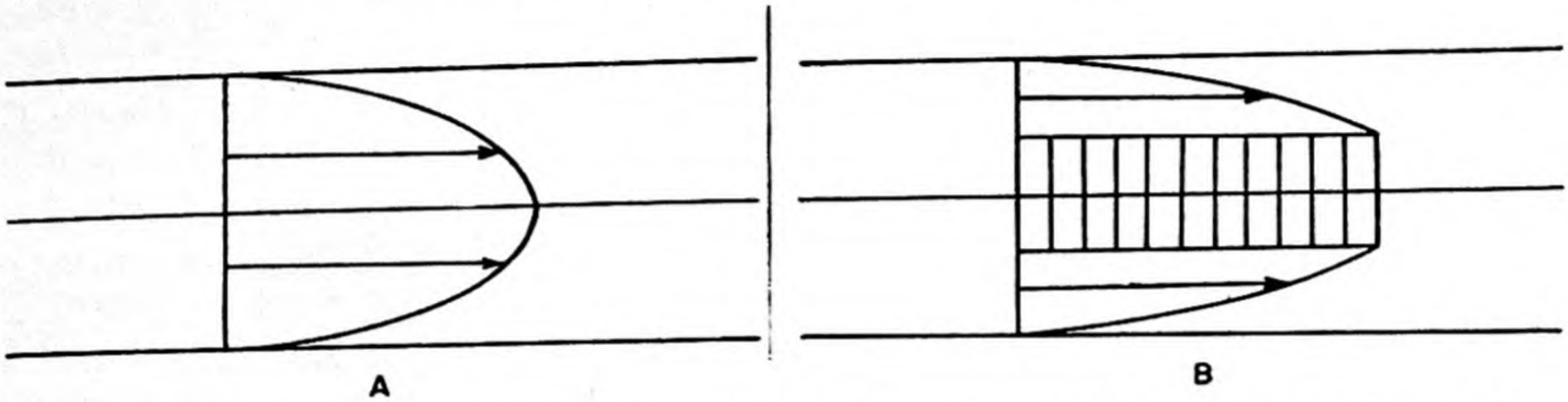


Figure II-5. Flow profiles in a capillary: (A) parabolic flow, with a Newtonian liquid; (B) plug flow, with an ideal plastic.

the radius of the capillary, and the density and the viscosity of the liquid. He derived the expression

$$R = 2Vrd/\eta \tag{5}$$

in which R is known as the Reynolds number. The critical value for R, a dimensionless number, is 1400 for Newtonian liquids, at which turbulence sets in. Turbulence is avoided by maintaining the velocity V of the liquid at such a level that R is well below 1400. In non-Newtonian liquids, however, the critical Reynolds number appears to be a function of the rate of shear and the size and shape of the molecules. Large elongated molecules decrease the critical value of the Reynolds number markedly.

In a Newtonian liquid showing laminar flow in a capillary, concentric cylindrical films of the liquid move past one another somewhat like the various segments of a collapsible telescope. The velocity distribution of the various layers is indicated in Figure II–5A, which

[4] O. Reynolds, *Phil. Trans.*, *A 174*, 935 (1883); *177*, 171 (1886).

shows a cross section of the capillary. It appears that the distribution curve is parabolic. The highest velocity is found in the center of the capillary whereas the speed is zero at the wall. From the shape of the curve it appears that the shearing stress, or velocity gradient, represented by the slope of the tangent at each point of the curve, is zero in the center of the capillary and greatest at the wall.

The velocity distribution for a Bingham body in a capillary is indicated in Figure II–5B. Near the wall, where a high shearing stress exists, a normal parabolic flow pattern is observed. Upon approaching the center of the capillary the shearing stress becomes smaller. Since the stress is zero in the center, there must be a point between the wall and the center of the capillary where the shearing stress is equal to the yield value. At any shearing stress below the yield value no laminar flow can exist in the Bingham body. Consequently a cylinder of the material moves more or less as a solid plug in the center of the capillary. By increasing the pressure the plug will decrease in diameter, but it will never disappear completely at any finite velocity of the liquid. By decreasing the pressure the unsheared plug will increase in diameter. At a certain pressure the shearing stress at the wall will have decreased so much that the yield value has been reached. At that point there is no longer any laminar flow in the capillary.

The mathematical solution of the problem of mixed flow in a capillary is exceedingly complicated and unsuitable for a practical experimental approach. Thus, capillary viscometers cannot be used advantageously to determine the fundamental rheological constants of the plastic inks.

2. Rotational Viscometer

In the rotational viscometer, an instrument conceived by Couette,[5] a liquid fills the annular space between two cylinders. One of the cylinders is rotated while the torque on the other is measured, usually as the angle of deflection of a torsion wire attached to the cylinder. Figure II–6 shows schematically a rotational viscometer of the conventional type in which the outer cylinder *A* rotates by means of the motor *M*, while the torque on the inner cylinder *B* is measured by means of the deflection of the torsion wire *W* provided with a dial *D*

[5] M. Couette, *Ann. chim. et phys.* (6), *21*, 433 (1890).

attached to a support E. Another accurate way of measuring the torsion is by means of an electrical strain gauge.

The mechanism of the flow of a plastic liquid in a rotational viscometer has been established by Reiner and Rivlin.[6] Consider an outer cylinder or cup with a radius r_c and an inner cylinder or bob with a radius r_b immersed in the liquid to a height h. Let M represent the total torque on the bob. At equilibrium in a liquid film of radius

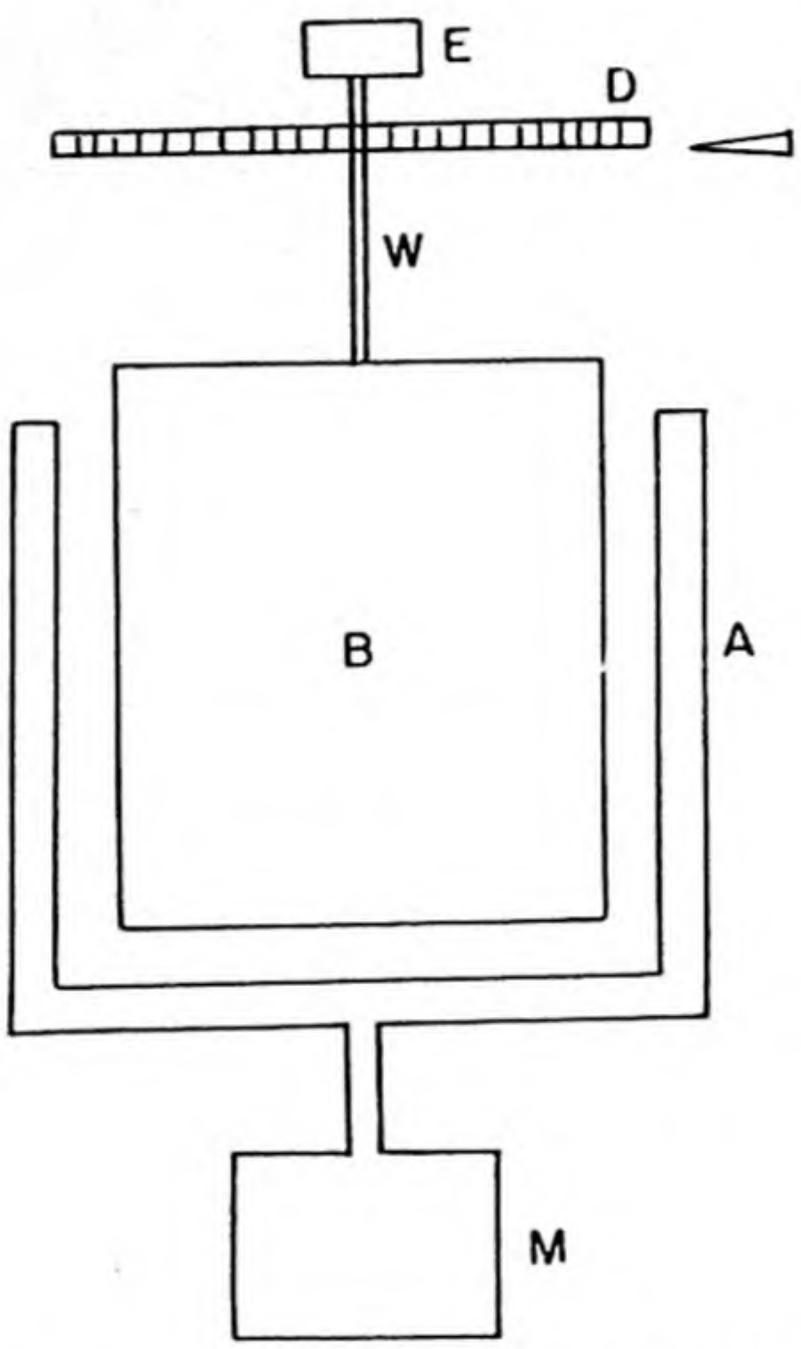


Figure II-6. Schematic representation of a rotational viscometer.

r the moment of the shearing force S taken over the total area must be equal to the torque M. Thus,

$$S \times r \times 2\pi rh = M \tag{6}$$

and

$$S = M/2\pi r^2 h \tag{7}$$

It thus appears that in the rotational viscometer the shearing stress is never zero, as in the center of a capillary viscometer, but always has a finite value. This then is the key to the application of the rotational viscometer for plastic liquids. If the precaution is taken of making the minimum shearing stress at the surface of the cup larger than the

[6] M. Reiner and R. Rivlin, *Kolloid-Z., 43,* 1 (1927).

yield value of the liquid, the entire plastic will be in laminar flow, and plug flow will be completely eliminated. The condition for laminar flow in the rotational viscometer is thus:

$$S_{min} = M/2\pi r_c^2 h \tag{8}$$

in which S_{min} represents the minimum shearing stress.

A rotational viscometer should have a small annular space. In that case the shearing stress is practically constant throughout the sample subject to stress, as may be seen from equation (6). This condition is never fulfilled in a capillary viscometer.

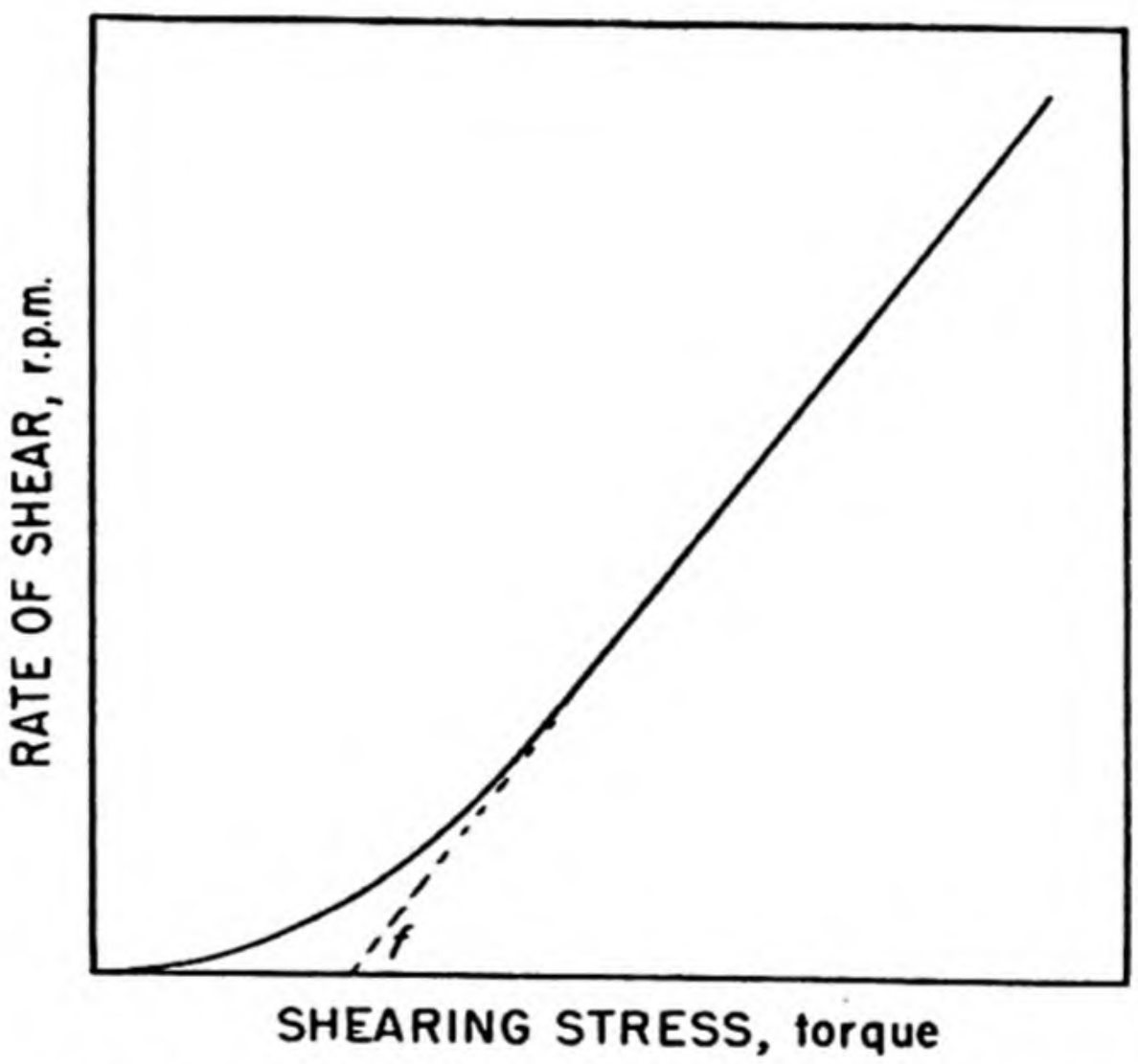


Figure II-7. Rheological diagram for a non-Newtonian liquid in a rotational viscometer.

A flow curve is obtained with a rotational viscometer by measuring the angular deflection of the bob at different cup speeds, usually obtained with a motor and a variable speed transmission or with a motor having an electronically controlled variable speed.

Plotting the values of the equilibrium shearing stress (torque) against the rate of shear (r.p.m.), a curve of the type shown in Figure II–7 generally is obtained for printing inks. The rheological diagram does not necessarily indicate that the ink is not an ideal plastic body, for the following reasons. At higher shearing stresses the force-flow relationship is linear. Upon continuously reducing the rate of shear the conditions for laminar flow, as expressed by equation (8), may

not be fulfilled and plug flow appears in the rotational viscometer. This makes it impossible to establish the complete rheological diagram for laminar flow. It is easy to see, however, that for a Bingham body the yield point is found by extrapolation of the straight part of the line until the torque axis is intersected. The corresponding torque is the yield value.

A Bingham body has, by definition, one single yield value. Yet, its rheological diagram in a rotational viscometer would indicate a lower, maximum, and a Bingham yield value, just as required, according to Houwink[7] for any nonideal plastic. In the Bingham body plug flow is responsible for this behavior. The lower yield value indicates the point where the outer layer of the plug starts laminar flow while the maximum yield value indicates the point where the entire plug has disappeared.

For a real plastic it is not very well possible to indicate whether the curved, lower part of the torque-r.p.m. relationship is caused by plug flow or whether this curvature is essentially the result of the flow properties of the plastic. One cannot, therefore, state unambiguously whether a plastic body has an ideal behavior and whether a Bingham yield value f_B is a physical reality. It has been found very useful, however, to consider plastic inks as Bingham bodies and to establish the yield value by extrapolation of the straight part of the line to zero stress. Whether or not ideal behavior is a physical reality or a mathematical simplification is irrelevant for the practical rheology of inks.

Reiner and Rivlin's theory indicates that the smaller the annular space between the cylinders, the less pronounced is the region of plug flow in the rotational viscometer. Actually one finds that with smaller annular spaces the region of the curvature in the S-D curves is reduced, making it more likely that inks may approach ideal plastic flow characteristics.

In Newtonian flow the coefficient of viscosity is defined unambiguously from equation (2) as

$$\eta = S/D \tag{9}$$

in view of the linear S-D relationship. For non-Newtonian liquids, where the S-D relationship is not linear, an apparent viscosity has

[7] R. Houwink, *Elasticity, Plasticity and the Structure of Matter*, Cambridge Univ. Press, London, 1937.

been indicated as the variable ratio between shearing stress and rate of shear for each given rate of shear. Such an apparent viscosity, however, has very little significance and may be utterly confusing. Its use, therefore, should be avoided.

A coefficient of plastic viscosity U may be defined, in analogy with the coefficient of viscosity, as the tangential shearing force per unit area in excess of the yield value which will produce the unit rate of shear. Its value may be found from the diagram of Figure II–7 as the cotangent of the angle of the straight part of the line with the torque axis. Thus,

$$U = (S - f)/D \tag{10}$$

D. VISCOSITY AND TEMPERATURE

The viscosity of liquids varies considerably with the temperature. In general the relation between viscosity and temperature may be expressed by the following equation:

$$\eta = ae^{b/T} \tag{11}$$

where a and b are constants, and T is the absolute temperature. For some liquids a temperature rise of 1°C. may reduce the viscosity as much as 20 per cent of its value. It is not surprising, therefore, that an adequate control of the temperature is essential in any viscosity measurement.

Control of the temperature is usually attained by immersing the viscometer in a water bath the temperature of which is thermostatically controlled. Such an arrangement is satisfactory for lower rates of shear, but at higher rates of shear it may lead to a marked discrepancy between the temperatures of the sheared liquid and the water bath. The reason for this discrepancy is that the energy required to shear the liquid is dissipated as heat, which, if it is not carried away rapidly enough by the cooling mechanism, will cause the temperature in the annular space to rise.

In the capillary viscometer the effect is small but by no means negligible, especially at higher rates of shear. Although in the capillary viscometer the liquid is subjected to the highest shearing stresses for only a short period of time, it must be realized that the highest rate of shear is near the wall of the capillary, where the velocity of the liquid is lowest. Thus, it was found that at stresses of 10^5–10^6 dynes per cm.^{2} in a capillary viscometer errors of at least 5 per cent

in the viscosity of oils were found to occur as a result of heat effects.[8]

Dissipated heat is a much more serious problem in a rotational viscometer where the same volume of liquid is sheared during the entire period of operation and a constant flow of heat takes place from the sheared liquid to the water bath. As a result the temperature of the liquid may rise several degrees above the temperature of the water bath.

If the torque of the viscometer is indicated by M it may be calculated that for each revolution an energy of $2\pi M$ is dissipated. At 500 r.p.m., for a torque value of 2×10^5 dynes per cm.^{2}, an average value for a viscous ink, an energy of 3×10^8 ergs per second is dissipated. If 3 cm.^{3} are sheared, an energy of 10^8 ergs per second per cm.^{3} of liquid is dissipated, corresponding to 2.4 g.-cal. Such an energy dissipation would markedly increase the temperature of inks, the specific heat of which is usually less than 0.5. For example, temperature rises up to 4°C. have been reported in a polybutylene oil of a viscosity of 145 poises sheared at a rate of shear of 440 reciprocal seconds.[9] Such a temperature rise will cause a drop in viscosity of about 40 poises, a deviation of more than 25 per cent. Successful viscometry at high shearing stresses, therefore, depends on adequate temperature control.

The temperature in the annular space in the rotational viscometer may be measured by building a resistance thermometer or a thermocouple into the stationary bob or into the rotating cup. Instead of keeping the water bath at a constant temperature, the temperature of the bath must be adjusted at each shearing stress at a value low enough to maintain a constant temperature in the sheared liquid. Lower[9] showed that for shearing stresses below 16,000 dynes per cm.^{2} temperature control was adequately maintained in a particular type of rotational viscometer by immersing the cup in a water bath. At shearing stresses between 16,000 and 50,000 dynes per cm.^{2} it was necessary to lower the bath temperature, while the sheared liquid was maintained at a constant temperature, as indicated, by a thermometer built in the bob. At still higher shearing stresses an additional temperature control point, built in the wall of the stationary cup, showed higher temperatures than the bob temperature, as a result of the higher shearing stresses at the cup wall. At these high stresses the

[8] D. Tollenaar and H. Bolthof, *Ind. Eng. Chem., 38,* 851 (1946).
[9] G. Lower, *Thesis,* Lehigh University, Bethlehem, Pa., 1950.

temperature should be maintained at an average value between that of the cup and that of the bob.

Failure to maintain an adequate temperature control will result in a distorted rheological diagram. For example, for a Newtonian liquid, instead of a straight line through the origin a curve is found somewhat similar to a pseudoplastic flow curve as shown in Figure II–3, curve *A*. The actual viscosity, decreasing at increasing shearing stress, is represented by the cotangent of the angle of the tangent in each point of the curve with the stress axis. Since actual temperature is unknown, the results are without significance. In the absence of adequate temperature control no true equilibrium sets in and the measured viscosity decreases slowly at a constant high rate of shear because of the temperature increase. As a result, curves obtained by increasing and decreasing rates of shear do not coincide but give rise to a loop in the rheological diagram which is meaningless.

From extensive investigations[10] at exceedingly high shearing stresses, up to 1.8×10^6 dynes per cm.^{2}, it appeared that straight mineral oils remain Newtonian at the highest shearing stresses. Long chain polymers, however, showed a marked decrease in viscosity at high stresses, most likely due to molecular orientation.

E. THIXOTROPY

It has been known for many years that the viscosity of certain dispersions may increase on standing. In 1927 Freundlich and Peterfi[11] introduced the term thixotropy, defined as an isothermal gel-sol transition. The authors already recognized that a mere increase and decrease in viscosity upon mechanical agitation and subsequent standing must also be considered as thixotropic behavior.

Thixotropy, or its apparent absence, is of great importance in inks, and will be discussed later. A desirable, high pigment loading is often prevented in inks by the occurrence of thixotropy. It is a phenomenon which is irrevocably connected with plasticity and non-Newtonian flow behavior. Newtonian flow is never accompanied by thixotropy, but plastic flow is impossible without thixotropic behavior, although the thixotropy is not always detected.

The physical significance of a yield value may be expressed as follows. While the rheological units of the liquid are immobilized by

[10] *Special Tech. Pub.* No. 111, A.S.T.M., Philadelphia, 1951.
[11] H. Freundlich, *Thixotropy*, Hermann, Paris, 1935.

cohesional forces at low shearing stresses, they will be liberated when the shearing stress exceeds the yield value. The tendency to reform the once broken-up structure, however, remains in existence as a result of attractive forces between the units, since the material is a plastic and never changes by shearing stresses into a Newtonian liquid.

The rebuilding of the broken-up structures, however, cannot take place instantaneously, but is necessarily a process of motion, alignment, and orientation of the rheological units. Such a process of rebuilding of the structure may require a small fraction of a second, an hour, or possibly even many months. If the rebuilding takes place within a few seconds, thixotropy is never recognized rheologically. However, other means, such as dielectric measurements, may clearly indicate a thixotropic behavior in such small periods of time and will be discussed later.

If the rebuilding of the structure, for example, takes weeks, a simple laboratory experiment of several hours' duration will hardly show the existence of thixotropy. If, however, the rebuilding occurs in the intermediate period, for example, of the order of an hour, thixotropy may be recognized by a simple rheological observation.

If the forces between the rheological units which form the structures responsible for thixotropy are very weak, then a very small shearing stress is already sufficient to break up the entire structure. Since rheological measurements are necessarily made on systems subjected to shear, in systems with very weak cohesive forces the measurement itself may therefore destroy the condition, and thixotropy is not recognized.[12]

It thus appears that the thixotropy always present in plastic systems is easily recognized only when the tendency to aggregation of the rheological units is neither very pronounced nor very weak, causing a rebuilding of the structure in an easily observable period of time. A rheological diagram of a thixotropic liquid taken rapidly with a rotational viscometer is shown in Figure II–8. In the rapid method of determining torque-r.p.m. relations nonequilibrium values are taken. The material is first subjected to a high shear to break up structures present at lower rates of shear. Upon rapidly decreasing the rate of shear the straight line *cda* is followed, indicating that

[12] A. Voet and L. Suriani, *J. Colloid Sci., 6,* 155 (1951).

in the period of a few minutes necessary for taking the measurement the structure is not rebuilt. The line *ao*, at a very low shearing stress, usually represents plug flow. After a predetermined period of rest, often ten minutes, the shearing stress is again increased. This time the line *obc* is followed, indicating the gradual destruction of structures subjected to increasing shearing stresses. The loop *obcd* in the diagram is therefore the result of thixotropic behavior. From the above it is obvious that a thixotropic loop is only observed when a thixotropic buildup occurs in a period of time easily within the limits

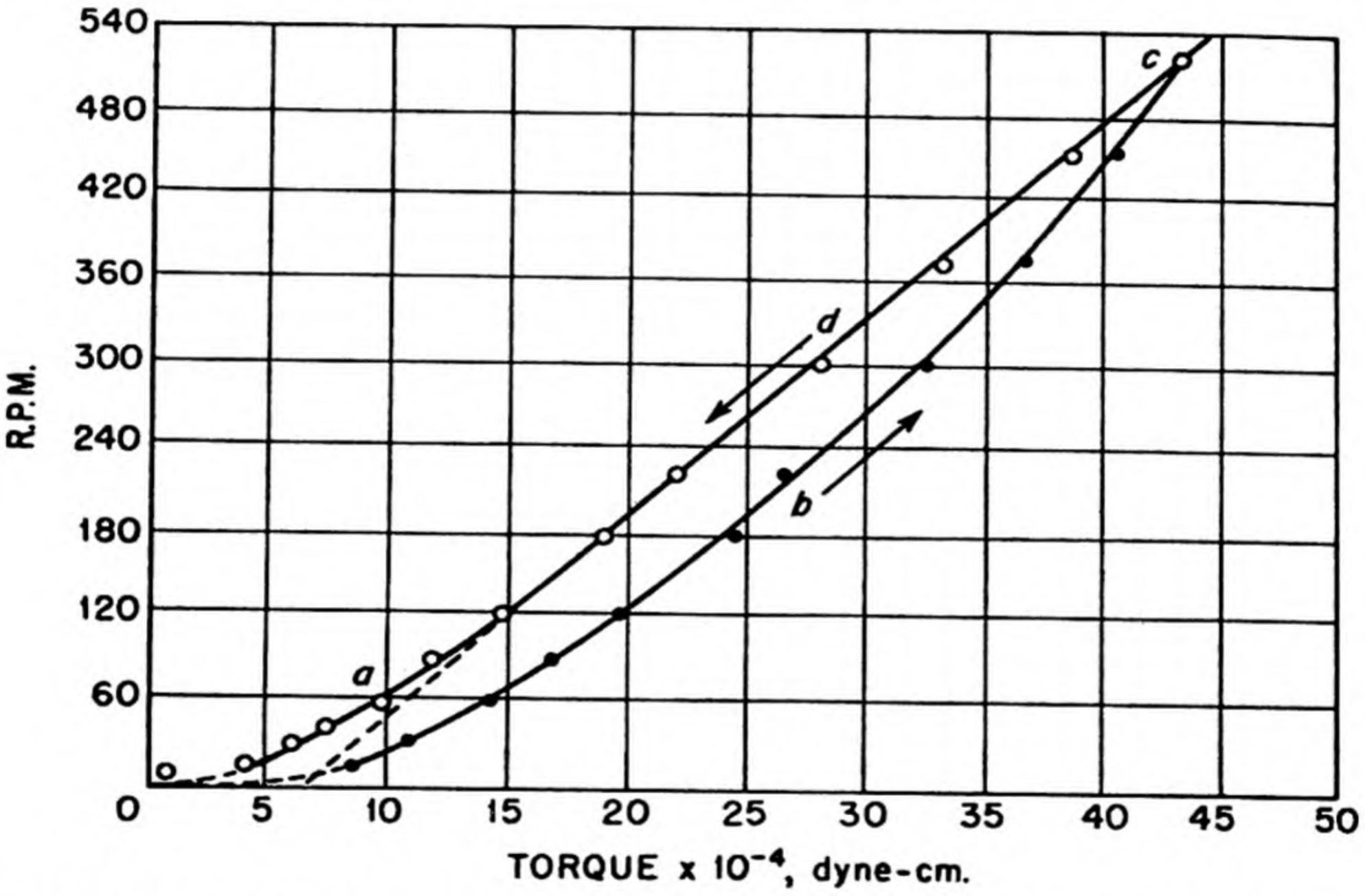


Figure II-8. Thixotropic behavior of typographic printing inks. Viscosity = 73.3 poises; yield value = 8300 dynes/cm.² at 30.0° C.

of a laboratory experiment. It is obvious that with this method neither a rapid rebuilding in a few seconds nor a slow rebuilding in a few days or weeks is detectable.

It appears that the thixotropic loop in a rheological diagram taken at constant temperature is practically indistinguishable from a rheological diagram observed for a nonthixotropic liquid in the absence of temperature control. The existence of thixotropy therefore may be derived only from a rheological diagram showing a loop if the temperature of the liquid in the annular space of the rotational viscometer is rigidly held constant. The absence of adequate tempera-

ture controls has led in the past to erroneous conclusions about thixotropic behavior of mineral oils at high shearing stresses.[13] Theoretically thixotropy can be studied most advantageously from a three-dimensional *D-S-t* plot (*t* = time), in which a rheological diagram, taken at times t_1, t_2 . . . t_n, represents cross sections perpendicular to the *t*-axis. In practical rheology the act of measurement affects the structure so markedly in the earlier stage of setting that significant *D-S-t* plots, independent of the instrument used, cannot be obtained. In the later stages elasticity in the gel makes it impossible to describe the phenomena adequately by a simple flow response to stress.

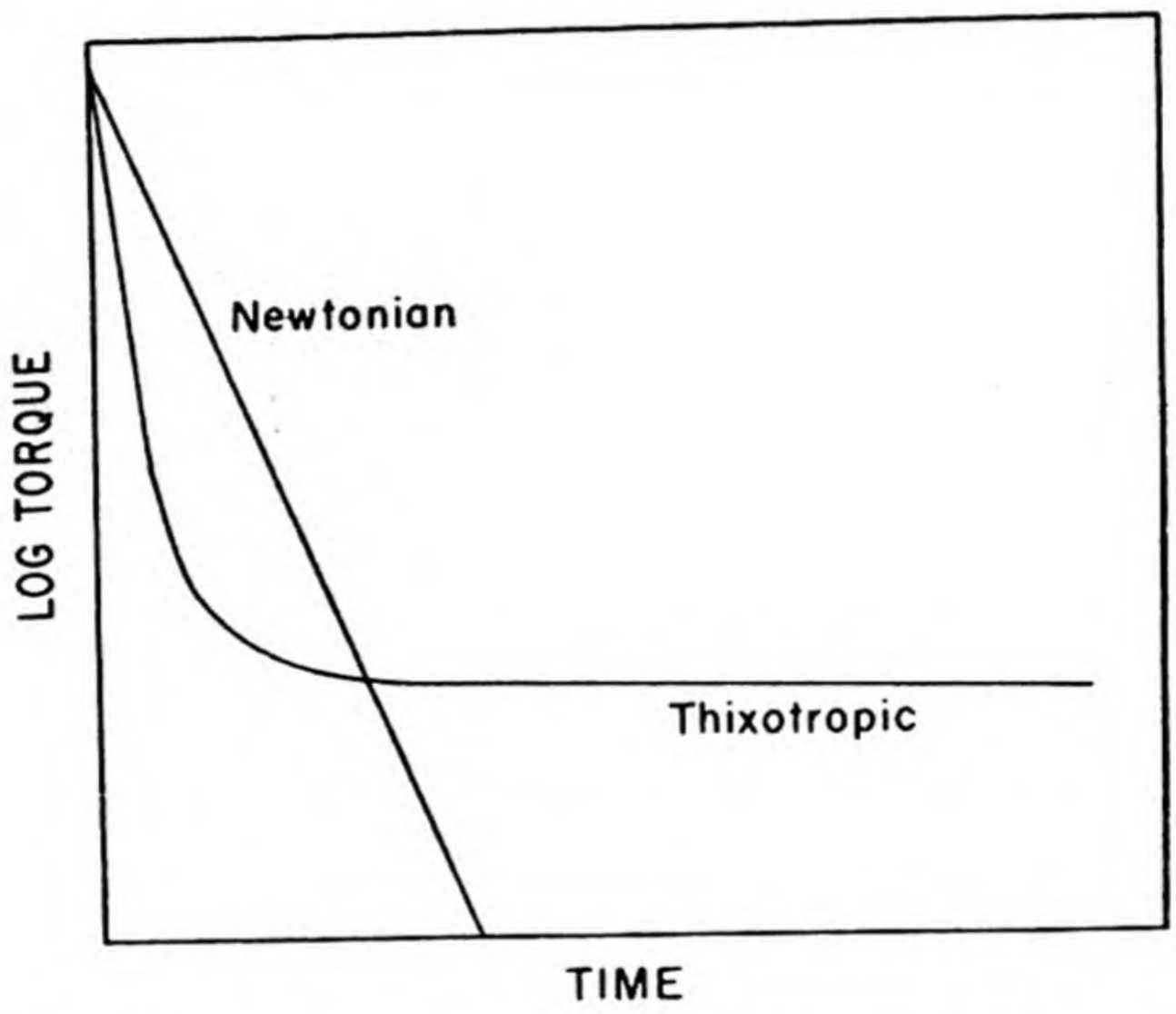


Figure II-9. Typical diagram of Bowles' empirical flow test.

In printing inks one is mostly concerned with thixotropy at rather low shearing stresses, as will be discussed later. The study of such thixotropic bodies is greatly hampered by the absence of fundamentally sound measuring methods which do not destroy the structure. Little is known about the completeness of the reversibility of the changes in flow response to stresses and about aging phenomena. The quantitative knowledge of the influence of other external factors is only rudimentary. The ink maker, therefore, has often relied on rather crude flow tests, such as inclined plate or spatula tests, in order to establish

[13] R. N. Weltmann, *Ind. Eng. Chem. Anal. Ed., 15,* 424 (1943).

whether the thixotropic properties of an ink are more marked than those of a standard with proven performance.

A more acceptable approach to the study of thixotropy in inks at low shearing stresses is made possible by the so-called empirical flow test.[14] In this method the motion of the inner cylinder of a rotational viscometer is observed under gradually decreasing torques, after the structure has been broken to a predetermined reproducible extent by rotation of the outer cylinder. For Newtonian liquids a straight line is obtained in a log torque–time plot, ending rapidly when the torque has declined to zero. Thixotropic materials show initially a behavior resembling a Newtonian liquid, but gradually a rigidity is developed which has the character of a yield value, as indicated in Figure II–9. The approach is essentially empirical, since no correlation with factors determining the internal structure of the dispersions has been established, but it is a notable improvement above conventional "spatula" tests.

[14] R. F. Bowles, *J.O.C.C.A., 31,* 87 (1948) ; *34,* 339 (1952).

CHAPTER III

FLOW OF DISPERSIONS

A. THEORETICAL CONSIDERATIONS

The coefficient of viscosity is an expression of the inner friction of a liquid, since its magnitude indicates the resistance which successive parallel layers of the liquid experience when moving along neighboring layers. The presence of dispersed material will influence the viscosity of the liquid.

A simple type of dispersion may be visualized as one in which there are rigid spherical particles, interacting neither with the liquid nor with one another. The particles of the dispersed phase are large enough not to experience Brownian motion but are small with respect to the dimensions of the viscometer. The effect of such particles upon the viscosity of the liquid is twofold. In the first place, it is obvious that no shear of liquid can possibly occur in the volume occupied by the rigid spheres. This effect tends to reduce the inner friction. On the other hand, a single particle, in view of its size, is subjected to the influence of different liquid layers, varying considerably in velocity. The spheres are caused to rotate and increase the internal friction of the surrounding liquid. A complete mathematical analysis of the frictional effects on the basis of hydrodynamics was made by Einstein[1] for laminar flow at a constant rate of shear, such as occurs in a rotational viscometer. The result may be expressed by the following relationship:

$$\eta = \eta_0(1 + kV) \tag{12}$$

whereby V is the volume concentration of the dispersed phase, while k is a constant calculated at 2.5. From the equation it appears that under the restrictions set forth not the particle size but the total volume of the dispersed phase is significant.

The relationship of equation (12) has been verified quantitatively. Eirich[2] found for dispersed glass spheres of different radii a value for

[1] A. Einstein, *Ann. Physik, 19* (4), 289 (1906); *34* (4), 591 (1911).
[2] F. Eirich, *Kolloid-Z., 74, 276* (1936); *81, 7* (1937).

k of 2.5 ± 0.2 by means of a rotational viscometer. Other experiments have shown that when the limiting conditions of Einstein's derivation of equation (12) are not rigidly adhered to the value of k is increased.

Although the equation is derived for flow at a constant rate of shear, it has been shown[3] that the equation retains its validity for Newtonian flow in a capillary viscometer.

If the particles are not rigid, deformation occurs, requiring energy, which causes a change in particle shape, resulting in a reduced viscosity. This effect is important only in emulsions. In the dispersions of solids which form printing inks, particle deformation by shear is not encountered.

A second, important deviation from Einstein's premises is the case of a dispersion of nonspherical particles. Many approaches have been reported in the literature, but the problem is so complex that no simple solution can be given. As a result of the velocity gradient in the liquid it appears that ellipsoidal particles will rotate, causing increased dissipation of energy and, therefore, increased viscosity.

Kuhn[4] found that for greatly elongated needle-shaped ellipsoids of an axis ratio f the constant k is increased and may be approximated by

$$k = 2.5 + (f^2/16) \tag{13}$$

For particles of a less pronounced shape the problem becomes very complicated, and a satisfactory solution has not been given for larger dispersed particles. The problem becomes exceedingly complex for heterodispersed systems and for particles of a more complicated shape. In each case, however, it is clear that the constant k is much larger than its value of 2.5 for spherical particles.

Another prerequisite for the validity of Einstein's equation is the lack of mutual interaction of particles, achieved only in very dilute dispersions. For electrically charged particles an additional resistance to flow is created by mutual repulsion of the particles, leading to an increase in the coefficient of viscosity. This phenomenon, known as electroviscous effect, has been calculated by von Smoluchowsky.[5]

[3] R. Simha, *Kolloid-Z.*, *76*, 16 (1938).
[4] W. Kuhn, *Kolloid-Z.*, *62*, 260 (1933); *68*, 2 (1934).
[5] M. von Smoluchowski, *Kolloid-Z.*, *18*, 190 (1916).

Of considerable interest is the problem of the viscosity of more concentrated dispersions subject to mutual particle interaction, which has received a great deal of attention. In general, the viscosity of such systems cannot be expressed by a linear relationship, but higher powers of the concentration enter into the equations. The viscosity function may be expanded in a power series as follows:

$$\eta = \eta_0(1 + k_1V + k_2V^2 + k_3V^3 + \ldots) \tag{14}$$

There have been attempts to make a hydrodynamical calculation of the constants k. The value of k is 2.5, in agreement with equation (12) as a limiting case. Guth found for k_2 the value 14.1, and Vand,[6] in an interesting approach, calculated its value at 7.35, in better accord with experiments. The ever increasing number of other theoretical approaches to this problem indicates that no definite solution has been found.[7]

If interaction between particles and vehicle occurs, Einstein's relation (12) is no longer valid. In the simplest approach such an interaction, known as solvation, is thought to cause a liquid film to be so tightly bound by the particle as to form a new kinetic unit of an increased volume. Consequently the total volume fraction of the freely moving units is larger than indicated by the actual volume of the dispersed phase, resulting in an increased viscosity. Since the actual volume of the dispersed phase is the only volume known, the factor k reflects the effect of the volume increase and becomes much larger than without solvation.

It must be stated that an "enmeshed" or "enclosed" dispersion medium does not increase the particle volume unless swelling of the particles takes place, a phenomenon not as a rule encountered in pigments. Particles which show complete or partly free draining of liquid through the pores do affect the viscosity markedly, as is found in dispersed high polymeric materials.

If particle structures are formed, enclosing or immobilizing larger parts of the dispersion medium, marked changes occur, leading to a non-Newtonian flow and ultimately to gelation.

[6] E. Guth *et al.*, *Kolloid-Z.*, *74*, 266 (1936). V. Vand, *J. Phys. & Colloid Chem.*, *52*, 277 (1948).

[7] J. Robinson, *J. Phys. & Colloid Chem.*, *53*, 1042 (1949); *55*, 455 (1951). M. Mooney, *J. Colloid Sci.*, *6*, 162 (1951). G. W. Lower, *Thesis*, Lehigh University, Bethlehem, Pa., 1950. R. H. Brailey, *Symposium on Printing Inks, A. C. S.*, New York, 1951.

The problem of the viscosity of concentrated dispersions of nonspherical particles is so complex that no attempts have been made to calculate the coefficients of the power series representing the dependency of viscosity upon concentration. Unfortunately, all inks are concentrated dispersions, generally of nonspherical particles or particle agglomerates. For these reasons there is very little in the theory of viscosity upon which one can rely for a quantitative prediction of viscosity of inks. Consequently the experimental approach is the only approach presently indicated to establish a more general relationship between viscosity and pigment concentration in inks.

B. VISCOSITY OF CONCENTRATED PIGMENT DISPERSIONS

1. Plastic Viscosity

The flow characteristics of inks are among their most important physical properties, and an understanding of the behavior of concentrated pigment dispersions is therefore essential. Since inks on the press are subjected to high shearing stresses, ink flow should be studied at high stresses. Consequently the plastic viscosity U, indicating the resistance to flow of inks subjected to high shear, is a physical constant of major significance in inks.

2. Influence of Pigment Concentration

In an extensive investigation, Voet and Suriani[7a] measured plastic viscosities of a series of commercial pigments dispersed in different vehicles at different concentrations. The measurements were made with the aid of a rotational viscometer. Care was taken to eliminate all temperature effects and to establish a true plastic viscosity value by means of equilibrium curves.

Figure III–1 indicates the result for dispersions of seven different kinds of pigments in linseed oil. The relative plastic viscosity U_R (ratio of plastic viscosity of the dispersion to vehicle viscosity) is plotted against the ratio of pigment volume to vehicle volume, ϕ. As may be seen from the figure, a linear relationship is obtained for each pigment dispersion in a semilogarithmic plot throughout the entire measured range, including the most concentrated dispersions obtainable. Similar results have been obtained with various other vehicles,

[7a] A. Voet and L. R. Suriani, *Am. Ink Maker, 30,* (4), 37 (1952).

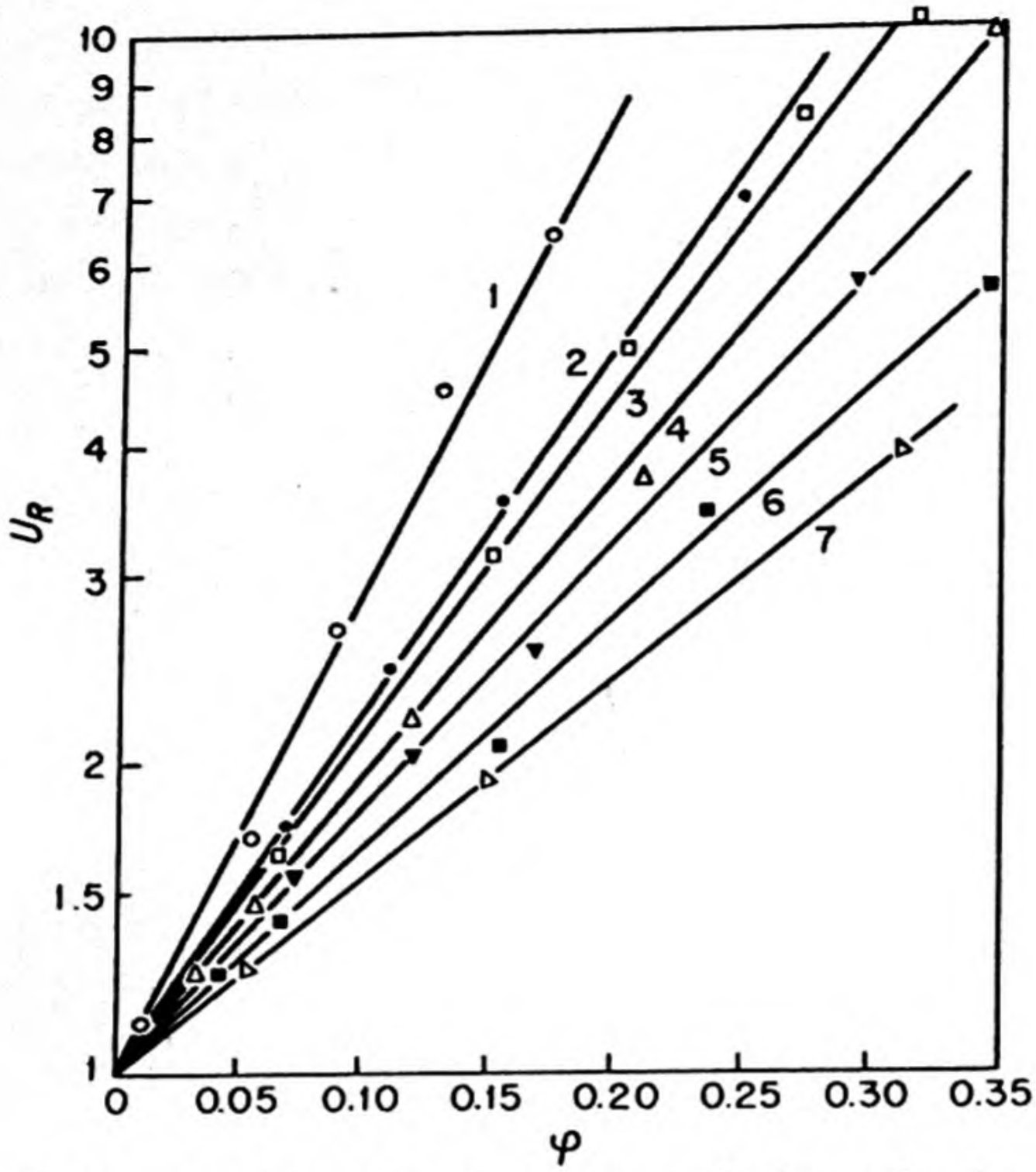


Figure III-1. Relationship between relative plastic viscosity U_R and ratio of pigment to vehicle volume φ for dispersions of pigments of varying concentrations in linseed oil: (1) channel black; (2) monastral blue; (3) barium lithol resinated; (4) milori blue; (5) barium lithol unresinated; (6) chrome yellow, medium; (7) benzidine yellow.

such as mineral oil, glycols, and resinous solutions. If the conventional volume fraction of the pigment were plotted against the relative plastic viscosity, no linear relationship would be obtained, indicating that the chosen relationship is likely to be more fundamental.

The following relationship was thus found to exist experimentally:

$$\log U_R = K\phi \tag{15}$$

or

$$U_R = \exp \{K\phi\} \tag{16}$$

whereby K is a constant.

The constant K, which represents the slope of the straight lines in the diagram, is thus the sole constant characterizing the rheological behavior of the dispersion. Table III–1 gives the values for the constant K as found for different pigments and different vehicles.

It thus appears that the plastic viscosity of an ink may be predicted from the viscosity of the vehicle and the pigment concentration, provided a characteristic constant K is known. The constant K for the most commonly used pigments in conventional vehicles has been determined, and a reasonably accurate prediction of ink viscosity is therefore possible.

TABLE III–1

Viscosity Constants for Different Pigments in Different Vehicles

Pigment	K for pigments dispersed in:			
	Glycol varnish	Linseed oil	Limed rosin varnish	Mineral oil
Benzidine yellow ..	6.31	4.38	3.11	4.78
Chrome yellow ...	6.62	4.93	2.59	4.50
Barium lithol (unresinated) ..	5.20	5.80	—	5.13
Ba lithol resinated .	5.99	7.34	2.91	6.89
Milori blue	4.81	6.44	4.37	7.07
Monastral blue	3.06	7.81	—	5.02
Channel black				
powder	6.58	10.4	4.22	10.2
pellets	3.92	7.08	3.51	5.31
Furnace black	4.84	6.68	3.71	7.11
Iron spheres	—	—	2.40	—

3. Relation with Theory

The relationship (16), found to be valid for the relative plastic viscosity, may be developed into a power series:

$$U_R = 1 + K\phi + \frac{K^2\phi^2}{2!} + \frac{K^3\phi^3}{3!} + \ . \ . \ . \qquad (17)$$

For low values of ϕ the higher terms may be neglected, and for dilute dispersions the following relationship must hold:

$$(U_R)_{\substack{\text{limit} \\ \phi = 0}} = 1 + K\phi \qquad (18)$$

Since for very low concentrations the dispersions exhibit Newtonian flow, the following relationship is valid at great dilution:

$$(U_R)_{\substack{\text{limit} \\ \phi = 0}} = \eta_R = 1 + K\phi \qquad (19)$$

and thus:

$$\eta = \eta_0(1 + K\phi) \qquad (20)$$

For infinite dilution ϕ and V coincide and it appears that the experimental constant K and the theoretical Einstein constant k of equation (12) are identical. From Table III–1 it may be found that for spherical particles of iron, showing no interaction with the limed rosin vehicle, the constant K was found to be 2.4, in satisfactory agreement with the theory. In general, however, K appears to be appreciably larger than 2.50, although of the same order of magnitude.

4. Particle-Vehicle Interaction

A closer examination of the data of Table III–1 shows that the constant K is not characteristic of the pigment alone, since its value varies for the same pigment in different vehicles. It seems, therefore, quite likely that interaction of pigment and vehicle, or solvation, occurs in the dispersions. Pigment particles may thus be surrounded with an immobilized film of liquid vehicle molecules. In this way the volume of the kinetically active units is increased, which reflects upon the constant K, as discussed previously. Since solvation differs for different pigment vehicle combinations, the influence upon K is not the same for each vehicle. For instance, K for channel black is high in nonpolar vehicles or in weakly polar vehicles, such as mineral oil or linseed oil, but lower in the presence of a strongly polar resin salt and a polar glycol vehicle. On the other hand, inorganic pigments, such as chrome yellow, exhibit an increased constant K in the strongly polar glycol vehicles. From the data, therefore, the general trend in variation of the constant K may be understood, but its quantitative prediction appears to be impossible at this time, and estimation of pigment viscosity has to rely upon the value of K as found by experiments. The relationship (15), however, which allows the quantitative prediction of the plastic viscosity of pigment dispersions from a single interaction constant, should prove to be valuable in printing ink technology.

C. PARTICLE AGGLOMERATION IN DISPERSIONS

1. Particle Agglomeration and Flow

A dilute dispersion in a Newtonian liquid generally shows a Newtonian flow behavior. Upon increasing the concentration of the dispersed phase, plastic flow is exhibited above a certain minimum concentration.

Plasticity is usually connected with particle structures, loosely connected clusters formed at rest and destroyed upon application of shear, to be rebuilt after discontinuation of the stress. Thixotropy occurs as a result of the time element involved in the re-forming of the particle clusters.

Although such agglomerated particle structures have been observed with a light microscope as well as with an electron microscope, such evidence is not quite convincing, since the objects viewed are usually in a completely different condition from the particles of the original dispersion. This is especially true in the case of electron microscopy. Methods other than optical observation, however, allow more direct conclusions about the condition of the particles in the dispersion.

2. Electrical Conductivity

An interesting approach to the study of particle agglomeration in conductive particles is the investigation of the electrical resistance. It was found[8] that the electrical resistance of a dispersion of carbon black in a mineral oil showed great variations, depending upon the type of black. For a 10 per cent by weight dispersion the d.c. resistance varied from 6.4×10^{11} ohms to 9.9×10^{6} ohms for different blacks at a potential difference of 100 volts. It was noted that the black with the greatest conductivity also imparted the least flow to the dispersion. Such differences in conductivity may be explained by considering the tendency to agglomeration of particles in the black, leading to the formation of structures. The so-called short blacks have a small particle size and a strong tendency to agglomeration, giving rise to particle networks, bridgelike structures of particle chains, throughout the dispersion. In such dispersions the electrical conductivity is predominantly of the electronic type. The electrons are able to move through the conductive black particles, which form bridges of particle chains. Long blacks, which have much larger particles and considerably less particles per gram than short blacks, do not have the tendency to form particle chains. The electrical conductivity, therefore, is predominantly of an ionic nature, by the motion of charged particles in the medium instead of by direct motion of electrons. Because of the difference of ionic and electronic conductance the electrical conductivity in long blacks may differ from

[8] F. H. Amon and O. J. Brown, Jr., *Am. Ink Maker, 19* (11), 25 (1941).

the conductivity in short blacks by as much as a factor 10^5.

The phenomena encountered in the study of the conductivity of carbon black dispersions clearly point to the existence of particle structures in short types of black. The study of conductivity, however, is not very well suitable for a quantitative approach to particle agglomeration.

3. Dielectric Properties of Dispersions

Ordinary light waves fail to penetrate more concentrated dispersions, but waves of a considerably lower frequency are not absorbed. Such waves, applied with the aid of electrical oscillators, are useful in the investigation of inks. Following this idea, pigment dispersions in organic vehicles have been subjected to electric waves of a fairly long wavelength. These waves are distorted upon passing through the materials investigated, and the degree of their distortion may be measured by suitable instruments. A proper interpretation of the data obtained yields information about the inner structure of the material investigated. This method is superior to the rheological approach, since electric waves of the proper wavelength will not destroy or even disturb the existing structural pattern in the printing ink.[9]

In the absence of electric or magnetic fields electric waves are propagated in vacuum without being disturbed. The presence of any material will distort the wave, owing to the action of the electric field on the electrons, dipoles, and particles in the material. A quantitative evaluation of the degree of the distortion of the electric wave by the material is found in the value of the dielectric constant, which may be defined as the ratio of the electric field strength in the absence and in the presence of the material. A simple way of determining the dielectric constant of a material is first to determine the capacity of a condenser with the plates separated by air and afterwards with the plates separated by the material under investigation. The dielectric constant of the material is equal to the ratio of the two capacities, since the influence of air is negligible.

The cell of a rotational viscometer consisting essentially of a properly insulated rotating cup and suspended bob may be used as the condenser. By this means dielectric as well as rheological measurements may be carried out simultaneously.

[9] A. Voet, *J. Phys. & Colloid Chem.*, *51*, 1037 (1947); *Am. Ink Maker*, *26* (6), 31 (1949).

The dielectric constant is characteristic of the material investigated and is influenced by the inner structure of the material. A study of the effect of the structure on the dielectric constant and the correlation of the changes in both dielectric constant and flow, as a result of shearing stresses, is desirable.

The problem of the distortion of electric waves by dispersed particles has been investigated theoretically. One of the more significant studies was made by Bruggeman,[10] who advanced a theory indicating the relationship between the dielectric constants of the dispersion, the vehicle, and the dispersed particles, as well as influence of concentration, size, and shape of the dispersed phase. It was found that the dielectric constant ϵ of a dispersion of particles of a dielectric constant ϵ_p dispersed in a volume fraction V in a medium of dielectric constant ϵ_m is independent of the size of the particles, but very dependent upon their shape. For a dispersion of spherical particles, regardless of their nature, the following relation was found to be valid:

$$1 - V = \frac{\epsilon_p - \epsilon}{\epsilon_p - \epsilon_m} \sqrt[3]{\frac{\epsilon_m}{\epsilon}} \tag{21}$$

When applied to systems in which the dispersed particles have an infinitely high dielectric constant, such as metals and carbon, this equation reduces to

$$\epsilon = \frac{\epsilon_m}{(1 - V)^3} \tag{22}$$

If the volume of the dispersed phase is less than 0.1, the higher terms of V may be neglected and the dielectric constant of the dispersion can be satisfactorily expressed by the approximate formula:

$$\epsilon = \epsilon_m(1 + 3V) \tag{23}$$

The dielectric constant of a dispersion of nonspherical particles may be considerably larger than the dielectric constant of spherical particles of the same concentration. The deviation from the spherical shape has the same effect as an increase in the volume of the dispersed pigment. For this reason it is necessary to introduce into the Bruggeman equation (23) a factor f, known as the form factor, which in effect increases the value of V. Equation (23) is then modified to

$$\epsilon = \epsilon_m(1 + 3fV) \tag{24}$$

[10] D. A. G. Bruggeman, *Ann. Physik, 24,* 636 (1935).

This procedure is justified by the experimental fact that the form factor appears to be independent of the vehicle, but depends exclusively on the particle shape. For spherical particles $f = 1$. For nonspherical particles f increases with the extent of deviation from spherical shape. It is obvious that only the form factor can account for changes in the dielectric constant of a system in which both the vehicle and the pigment are not changed in volume.

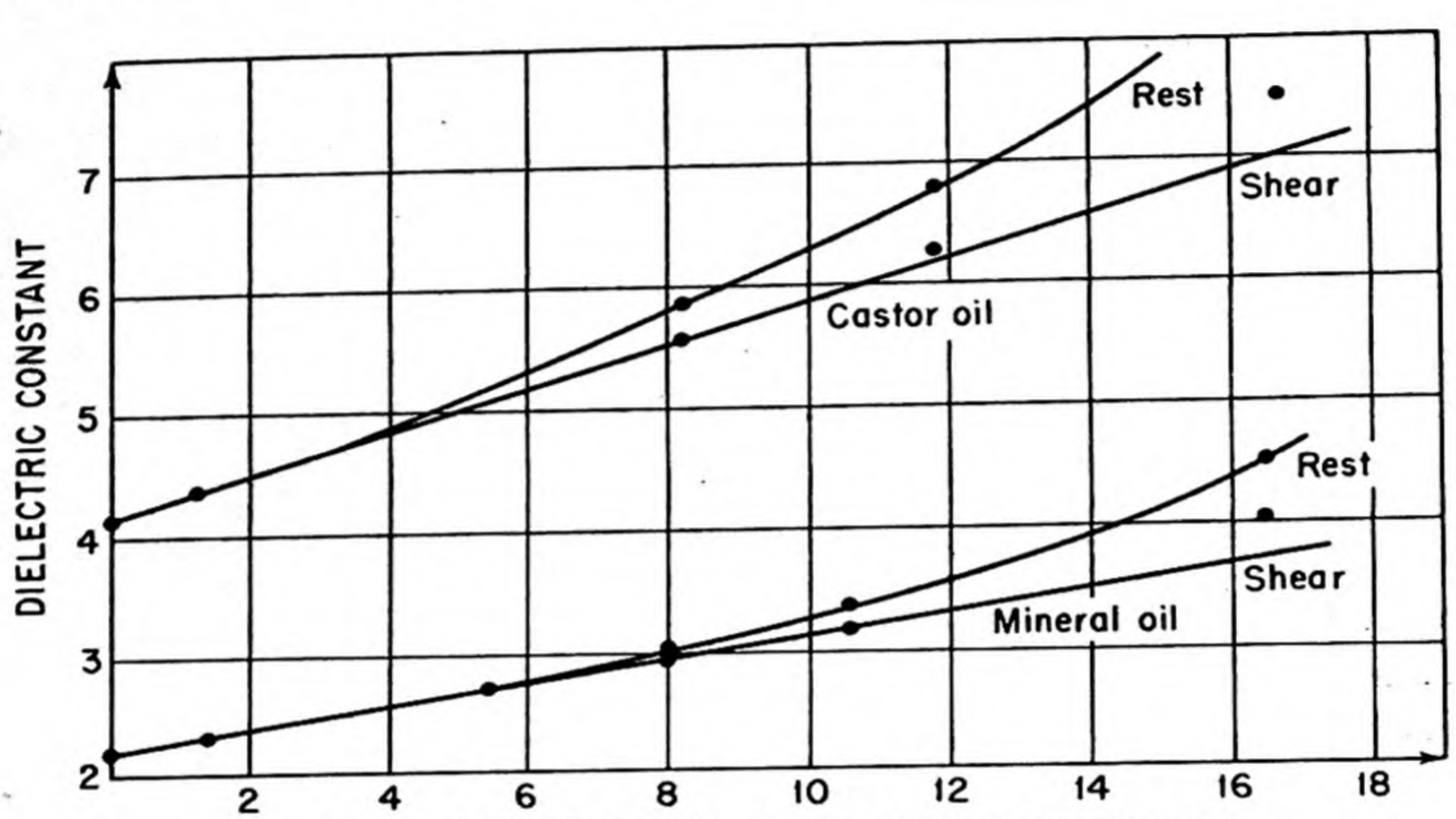


Figure III-2. Dielectric constants of zinc powder dispersions of varying concentrations.

The form factor for platelike or needle-shaped particles also depends on their orientation. The dielectric constant is largest when the orientation of the particles is parallel to the electric field, whereas a minimum value is found with orientation perpendicular to the field.

Figure III–2 shows the change of the dielectric constant with the concentration by volume of a dispersion of zinc powder of a near-spherical shape in different vehicles. For each vehicle the relationship is given by two lines, one representing a state of rest and another representing a state of agitation or shear. It was found experimentally that the dielectric constant for either vehicle in the state of shear may be represented by the relationship:

$$\epsilon = \epsilon_m(1 + 4.2V) \tag{25}$$

Comparing these results with equation (22) we find that an excellent correlation exists for the case of a form factor $f = 1.4$, indicating a slight departure from the spherical particle shape, as expected from microscopic observations.

It must be pointed out that at higher concentrations, for a system allowed to remain undisturbed after discontinuation of agitation, the dielectric constant increases rapidly, until it reaches the maximum value, indicated in the "rest" curve. Upon being again subjected to shear, the system returns to the linear dielectric constant-concentration relationship indicated by the "shear" line. The changes may be repeated at will and are completely reversible.

It is quite obvious that the increase in dielectric constant of the system is due only to an increase in the value of the form factor f, resulting from a change in shape of the existing dispersed units in the system. Such changes occur only as a result of particle agglomeration, since solid zinc particles occupying a constant volume in the dispersion cannot change their individual shapes as a result of the fairly mild agitation in the liquid. The newly formed particle cluster or agglomerate, however, has a shape different from the near-spherical individual zinc particle and is usually built up by a linear chain of individual particles, causing a rise in dielectric constant. Upon being subjected to shear, however, the agglomerates are destroyed and the original condition is restored.

It may be noticed that agglomeration occurs only at concentrations above a certain minimum concentration of the dispersed phase.

Rheological data indicate that all dispersions showing agglomeration have a non-Newtonian, plastic flow behavior, whereas all the more dilute dispersions, in the absence of particle agglomeration, show Newtonian flow.

The magnitude of agglomeration may be indicated by means of an agglomeration factor introduced as a change in form factor resulting from particle agglomeration. This agglomeration factor a_V for any volume V of pigment may thus be found from the ratio of the form factor at rest to the form factor in sheared dispersions.

The time necessary to build agglomerates may be determined accurately from the change in dielectric constant with time. For example, it was found that in dispersions of zinc powder in castor oil the changes are completed in a period of time ranging from a few seconds

to a minute, depending upon the concentration of the zinc particles. Such changes are generally too short to be detected rheologically, and therefore if rheological means of investigation were used, the system would be considered a nonthixotropic plastic. Actually, however, the system is clearly thixotropic, but with a short time factor.

The experiments carried out with zinc powder were repeated with a number of other materials, such as metal powders, titanium dioxide, and other organic and inorganic pigments, and especially with carbon black.

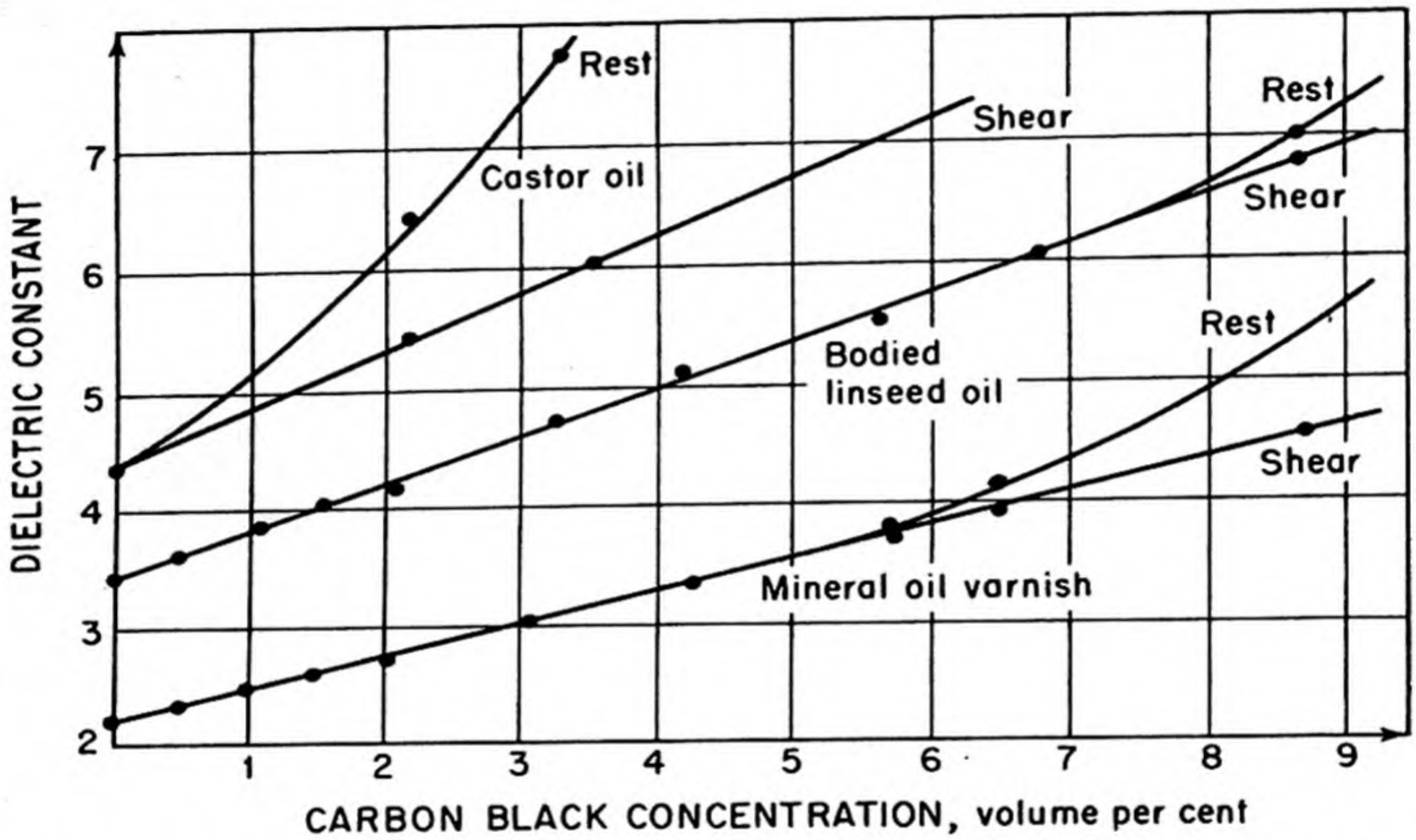


Figure III-3. Dielectric constants of dispersions of carbon black of varying concentrations.

Figure III–3 shows the change of dielectric constant with concentration for a dispersion of a channel black in three different vehicles.

Linear relations exist for the condition of shear, characterized by the following equation:

$$\epsilon = \epsilon_m(1 + 11.6V) \tag{26}$$

regardless of the vehicle. This indicates a form factor of 3.9, a deviation from the spherical shape for the units of carbon existing in the dispersion.

While electron micrographs always show spherically shaped elementary particles of carbon black, ordinary photomicrographs of

commercial black inks show beyond doubt that the kinetic unit in the vehicle is actually a nonspherical cluster of perhaps thousands of elementary particles. In time these clusters agglomerate at higher concentrations to form particle chains upon standing, as may be observed from the differences between rest and shear values of the dielectric constant.

From Figure III–3 it may be seen that even at very low concentrations of carbon black in castor oil the form factor is increased at rest, indicating pigment agglomeration. In the mineral oil vehicle no agglomeration is observed at lower carbon black concentrations, and only above 4 per cent by volume does particle agglomeration occur.

Agglomeration becomes apparent in linseed oil only in carbon black concentrations above 7 per cent by volume. Thus, we observe that the vehicle greatly influences the formation of particle agglomerates. Paint and printing ink technologists have known that this quality of a vehicle exists and have often referred to it as "wetting and dispersing" characteristics. The significance of the quality actually appears to reside in its power to prevent agglomeration of already dispersed particles.

A very pronounced thixotropy, characterized by a time factor of hours and even days, is found in most heatset inks. The thixotropic inks show a typical gel structure, which breaks upon agitation to form a very fluid ink, only to return to the solid gel upon standing. A similar behavior is shown by inks in which a very large percentage of resin is incorporated.

The dielectric changes which occur when subjecting these inks to shearing stresses were found to be slight. This indicates that a second type of thixotropy exists, not accompanied, as in the first type, by marked dielectric changes. On the basis of marked difference in setting time the existence of two distinct types of thixotropy had already been recognized in the literature.

Further investigations showed that the first type of thixotropy is characterized by a short setting time and by large dielectric changes, resulting from the formation of a particle structure built up by agglomerated pigment particles. The second type of thixotropy, characterized by a much longer setting time and by small dielectric changes, is accompanied by a more rigid gel structure, consisting essentially of a network of individual pigment particles placed at a short distance from each other and separated by resinous particles. The break-

ing up of this structure causes pronounced rheological changes, but does not result in marked dielectric changes, since the pigment particles, being separated by nonconductive resin, are not present in electrically conductive clusters. They are therefore difficult to distinguish electrically from completely separate particles.

Dispersions of particles of a dielectric constant which is not greatly different from the dielectric constant of the vehicle show a dielectric behavior similar to that of the systems discussed above. Examples are dispersions of organic pigments in oils. The effects, however, are small and the accuracy obtained in these investigations does not permit the establishment of definite agglomeration values indicating the degree of flocculation of the pigment.[11]

The relation between direct observation of flocculation by means of microscopic or electron-microscopic methods and rheological properties, electrical conductivity, and dielectric constant of pigment dispersions has been studied by Kinsman and Bowles.[12] The importance of the dielectric method of investigation appears clearly from this work.

[11] A. Voet and L. R. Suriani, *J. Colloid Sci., 7*, 1 (1952).
[12] R. G. Kinsman and R. F. Bowles, *J.O.C.C.A., 34*, 378, 592 (1951).

CHAPTER IV

FLOW OF INK BETWEEN PARALLEL PLATES

A. GENERAL TYPES OF FLOW

The rotational viscometer is the only instrument available for the rational evaluation of the flow properties of plastic inks. A satisfactory rotational viscometer, however, is too complicated for a control instrument.

A simple apparatus known as a spreadometer and based upon the principle of ink flow between parallel plates permits a rapid, accurate, and reproducible numerical evaluation of ink at low shearing stresses. It permits control of ink flow, but does not allow prediction of ink behavior on the press, where much higher shearing stresses prevail.

From a general study of flow phenomena of plastic bodies between parallel plates it appears that the change of distance between the plates with time is a valuable indication of the rheological characteristics of the flowing materials. A mathematical analysis of the data obtained makes it possible to differentiate between various types of flow, such as Newtonian, pseudoplastic, and ideal or nonideal plastic, and to establish a quantitative measure for the degree of resistance to deformation shown by the liquid or plastic bodies. The general procedure is to plot the change of plate distance with time against the plate distance in a logarithmic system of coordinates. If the relationship obtained is linear, the material has no yield value. From the actual value of the slope it may be established whether the material is Newtonian or pseudoplastic. If the relationship obtained is not linear, a yield value must be present. The character of the curves may generally be related to the values of the characteristic rheological constants of the materials investigated. Explicit relationships between applied force and resultant flow have been obtained only for a limited number of specific patterns of flow, such as Newtonian, pseudoplastic, or Bingham body.

B. APPLICATION TO INKS

A schematic representation of the principle involved in the spreadometer is given in Figure IV–1, where a drop of ink is placed on the

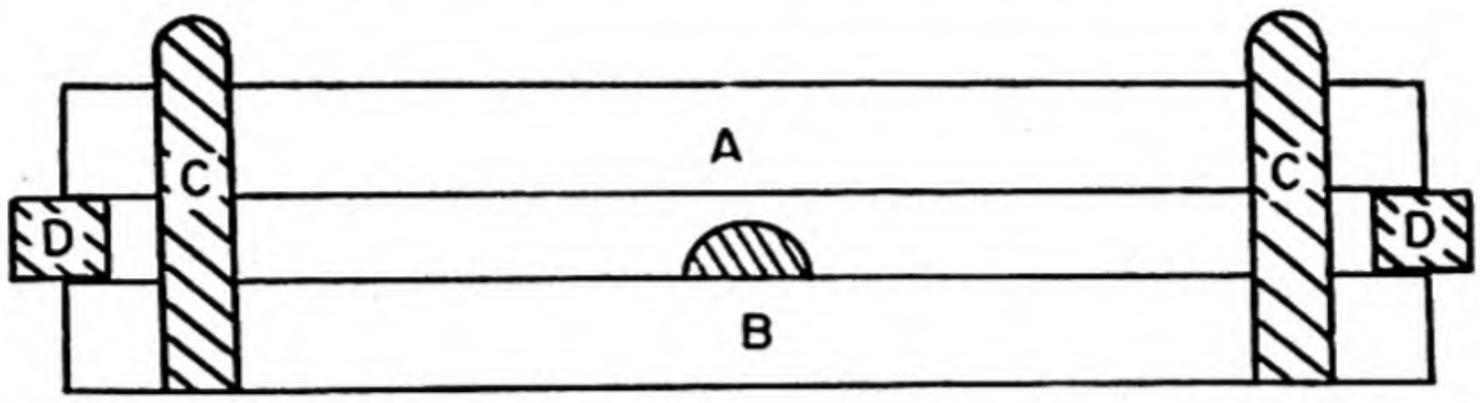


Figure IV-1. Schematic representation of the spreadometer principle.

bottom plate *B* of two parallel plates. A transparent glass or plastic plate *A* is placed on the drop of ink by removing the blocks *D*. The motion of plate *A* is guided by rods *C* and results in the spreading of the drop, first rapidly and gradually more slowly. The diameter of the drop is measured at varying time intervals by means of a scale engraved on the bottom plate.

In the original investigation improved accuracy was obtained by placing the drop in the center of a photographic enlarger, thus projecting the enlarged drop on a screen and making possible a very accurate estimation of the drop diameter. The top plate was released electromagnetically, while an electric timer, automatically set in motion upon release of the plate, permitted a more accurate timing.[1]

Figure IV–2 indicates the relationship between optically en-

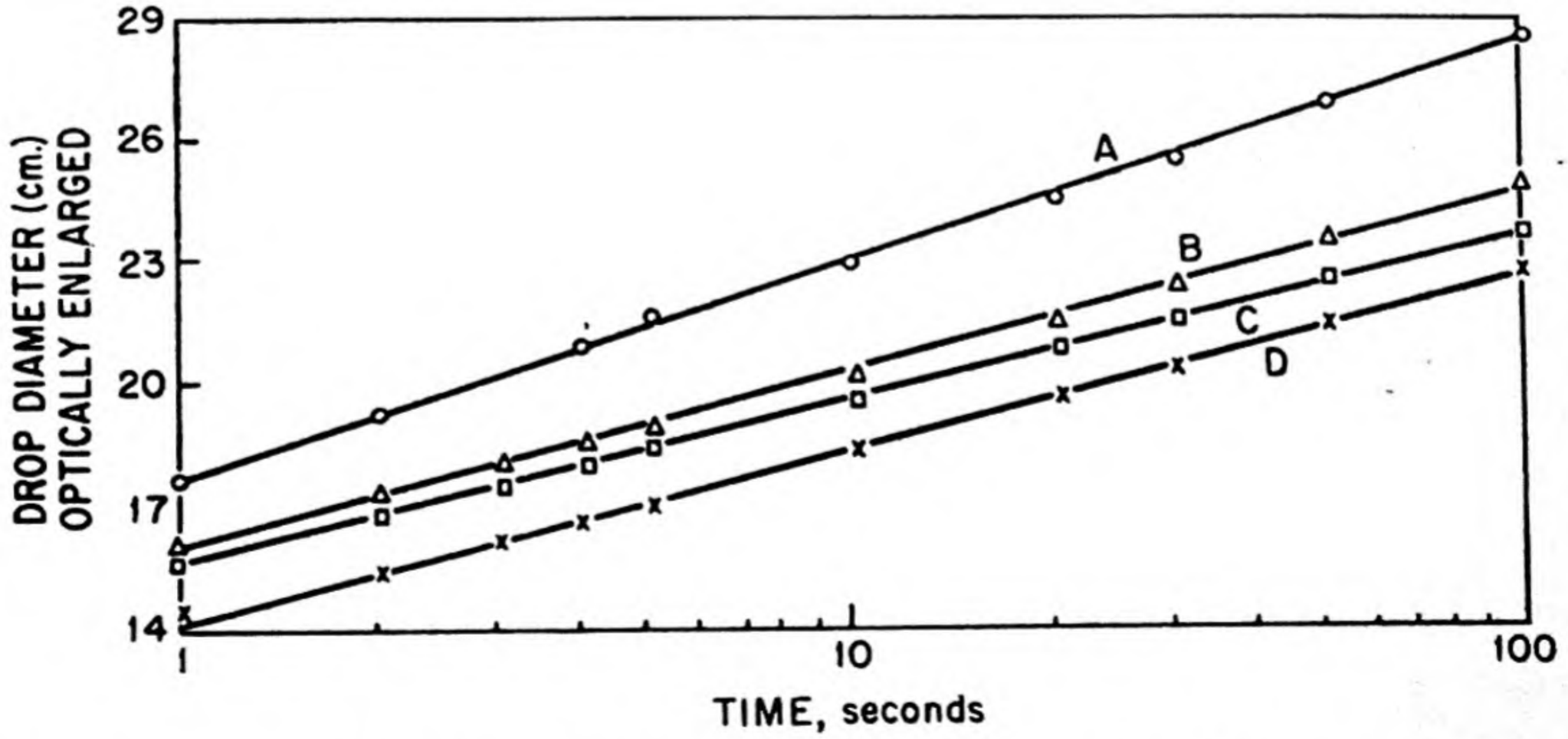


Figure IV-2. Relation between drop diameter and time in a spreadometer.

[1] A. Voet and J. S. Brand, *Am. Ink Maker, 28* (9), 28 (1950).

larged drop diameters and elapsed time, plotted in a semilogarithmic plot for a number of heavy news inks of various viscosities. It may be seen that throughout the entire time interval the relationship is, within the accuracy of the experiments, perfectly linear. The lines may thus be represented accurately by their intercepts on the ordinate

TABLE IV–1

Plastometer and Viscometer Data

Ink	Plastometer, temp. 25°C.		Rotational viscometer, temp. 30°C.	
	Intercept *I*	Slope *S*	Plastic viscosity, poises	Yield value, dynes/cm.²
A	17.6	5.4	55	870
B	16.1	4.3	95	5600
C	15.8	3.9	121	5610
D	14.4	4.1	192	6840

I and by their slopes *S*, defined as the tangents of the angles of the lines with the abscissas. The values are given in Table IV–1 which at the same time shows rheological characteristics as measured by means of a high-speed rotational viscometer. The slope of the straight part of the torque-r.p.m. curve is indicated as plastic viscosity, while

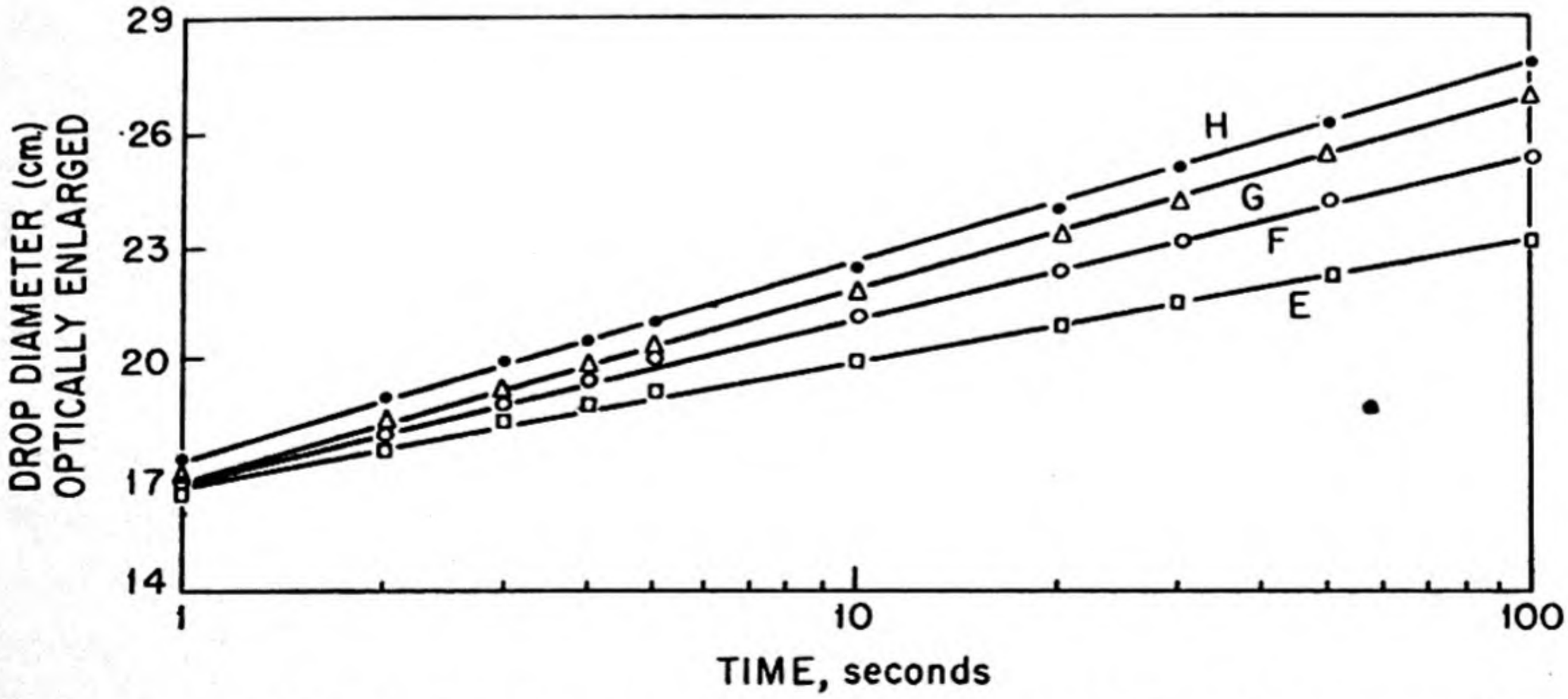


Figure IV-3. Relationship between drop diameter and time in a spreadometer.

the intercept of the extrapolated straight part of the curve on the torque axis is taken as yield value.

Figure IV–3 shows the relationship between drop diameters and logarithm of elapsed time for a group of viscous inks of comparable

viscosities. Again linear functions were found to exist. Table IV–2 shows intercepts and slopes as well as fundamental rheological properties.

The importance of using the proposed semilogarithmic method of plotting rather than the conventional logarithmic plots for printing inks appears clearly from the established linearity in the former method. In order to find out whether this linearity persists after longer periods of time ink drop diameters were measured accurately, by means of the optical system, for periods of time as long as two hours. The linearity between drop diameter and logarithm of the elapsed time was found to be maintained perfectly if enough ink was present.

TABLE IV–2

Plastometer and Viscometer Data

Ink	Plastometer, temp. 25°C.		Rotational viscometer, temp. 30°C.	
	Intercept *I*	Slope *S*	Plastic viscosity, poises	Yield value, dynes/cm.²
E	16.7	3.3	57	4570
F	16.8	4.3	52	4030
G	17.0	4.9	50	1560
H	17.4	5.3	47	2640

The linear functions found to exist for most printing inks make it extremely simple to establish the complete relationship by two measurements only, at convenient time intervals. It is therefore unnecessary to determine the drop diameter at very short periods of time after the release of the plate. For instance, measurements after 10 and 100 seconds should be sufficient to establish the complete relationship, although to improve the accuracy it may be desirable to determine more points of the line.

The significance of the established linearity for the measuring technique is now evident. Not being faced with the necessity of measuring drop diameters accurately after a period of time as short as one or two seconds, when the rate of extension of the drop is very large, one may dispense with the optical enlarging system. Drop diameters may be measured directly, without a projector, after longer time intervals, when the drop extension is proceeding slowly. Conse-

quently, most other measurements with the parallel plate plastometer have been made directly, by means of a scale scribed on the top plate of the instrument, without an enlarged projected drop image. Occasional checks with optically enlarged drops showed that the accuracy obtained by direct observation is quite satisfactory. For control purposes, therefore, the use of the optical enlarging system may be eliminated, in favor of the use of an exceedingly simple instrument for the measurement of the flow characteristics of heavy inks.

C. SLOPE AND INTERCEPT

It was found that the intercept increases with increased loading, carried out by adding weight to the top plate. Temperature increases always lead to a markedly increased intercept, but not always in the same manner for different inks. Some inks show decreased slopes; others are hardly affected.

Ink volume has a marked influence. For small quantities of ink a saturation value exists above which the drop diameter increase is less than predicted from the linear relationship in the semilogarithmic plot. For a very small quantity of ink the flow of the drop stops altogether. Thus a minimum drop volume is required to insure flow.

Flow properties of Newtonian liquids, characterized by a linear relationship between shearing stress and velocity gradient, were measured in the parallel plate viscometer. A mineral oil of a viscosity of 40 poises at 25°C., showing a Newtonian type of flow in the rotational viscometer, was investigated. It appeared that the relationship between drop diameter and logarithm of the elapsed time is not linear, but a curve convex to the time axis. When plotted in a complete logarithmic plot, however, all Newtonian liquids show a straight line, indicating a linear relationship between the logarithm of the drop diameter and the logarithm of the elapsed time.

Printing inks of a low viscosity, such as high-speed news inks with low pigment content and a thin vehicle, do not differ greatly from Newtonian liquids. Such inks show a deviation from the linear relationship in a semilogarithmic as well as in the complete logarithmic plot. However, as the pigment content increases, the behavior of these inks resembles less and less the Newtonian type, and the curves in the semilogarithmic plot more nearly approach a straight line.

Newtonian liquids, when allowed to flow between the plates of

a parallel plate viscometer, do not stop flowing at any drop diameter, but tend to spread indefinitely and eventually flow from the plates. This behavior is not found in printing inks, where the drop diameter does not extend beyond a definite limit.

D. YIELD VALUE

Theoretical considerations show that for a Newtonian liquid the shearing stress is zero in a parallel plate viscometer at every point of an imaginary plane midway between the plates. It gradually increases, as a parabolic tangent, until its maximum value is reached at the surface of the plates. For an ideal plastic the shearing stress is always below the yield value in a volume element of the liquid extending for some distance on both sides of the middle plane. Here no laminar flow can exist, and the liquid in this volume element moves as a solid amidst other parts of the liquid showing laminar flow. This phenomenon is the previously discussed plug flow.

The shearing stress decreases rapidly toward the center of a drop and appears to be directly proportional to the distance from the center. In a Newtonian liquid the maximum shearing stress will have a positive value at the surface of the plate at any drop diameter, causing liquid flow for an indefinite period of time. In an ideal plastic, however, the volume of ink subject to laminar flow gradually decreases at decreasing shearing stresses and finally disappears completely. At this moment, which is reached when the maximum shearing stress is equal to the yield value, flow ceases completely and the drop diameter reaches its maximum value.

The yield value f may be calculated from the maximum drop diameter D_m by means of the following relationship:

$$f = 12PV/\pi D_m^3 \qquad (27)$$

wherein P is the total loading and V the drop volume. Thus, for an ink of a maximum drop diameter of 5 cm. and a volume of 0.5 ml., at a loading of 115 g., a yield value of 1.7×10^3 dynes per cm.^{2} was calculated.

In thixotropic inks with a short setting time, this picture may be obscured somewhat if a marked structural buildup occurs in the ink during the measurements. For different loadings, different shearing stresses exist at a given distance from the center of the drop. This leads to different yield values, although each yield value is

characteristic of the state of structural buildup in the ink at the moment of cessation of flow.

A closer examination of data of Tables IV–1 and IV–2 shows beyond doubt that the intercept I on the ordinate at a given loading, for a given ink volume, is indicative of the ink viscosity. The lower the intercept, the higher the plastic viscosity, while a higher intercept corresponds to a lower plastic viscosity.

An examination of the data of Table IV–2 shows that inks E, F, G, and H do not differ greatly in plastic viscosity and therefore have similar intercepts. They vary, however, considerably in the slopes. A study of these inks and other data obtained with the parallel plate viscometer indicate that the slopes are related to an ink characteristic usually referred to as "shortness" or "length," a quality sometimes estimated by the length of ink thread which can be stretched between two surfaces without breaking. This property is related to the structural buildup in the inks. Shortness and length cannot be measured directly in fundamental units. Their magnitude seems related to the ratio of yield value to plastic viscosity.

Inks E, F, G, and H of Table IV–2 and Figure IV–3 are increasingly longer and show an increasingly larger slope. As a rule, the shorter the inks are, the smaller the slope.

The parallel plate viscometer permits the measurement of three constants, namely, intercept, slope, and ultimate diameter. The intercept must be considered as the most important constant, being directly related to ink viscosity. The slope may be judged to be next in importance, giving some indication of length or shortness under a low shearing stress. Finally, the ultimate drop diameter, leading to a yield value, may not have direct implications in the behavior of the ink during printing, but may be related to the leveling out of inks in the fountain in the absence of shearing stresses. Generally, however, intercept and slope will characterize the ink sufficiently for most purposes.

E. SPREADOMETER FOR CONTROL OF INK FLOW

The spreadometer, easily constructed yet rugged for plant control, may be used as a simple and comparatively accurate instrument for the measurement of ink flow.

Inks are measured volumetrically by means of a plunger which

pushes exactly 0.50 ml. of ink from a cylindrical opening in the bottom plate and places it in the center of the plate. Release of the top plate occurs automatically upon pushing the plunger upwards. Temperature control may be effected by the use of a hollow bottom through which water of constant temperature circulates. A schematic representation of the instrument as used for ink flow control is given in Figure IV–4.

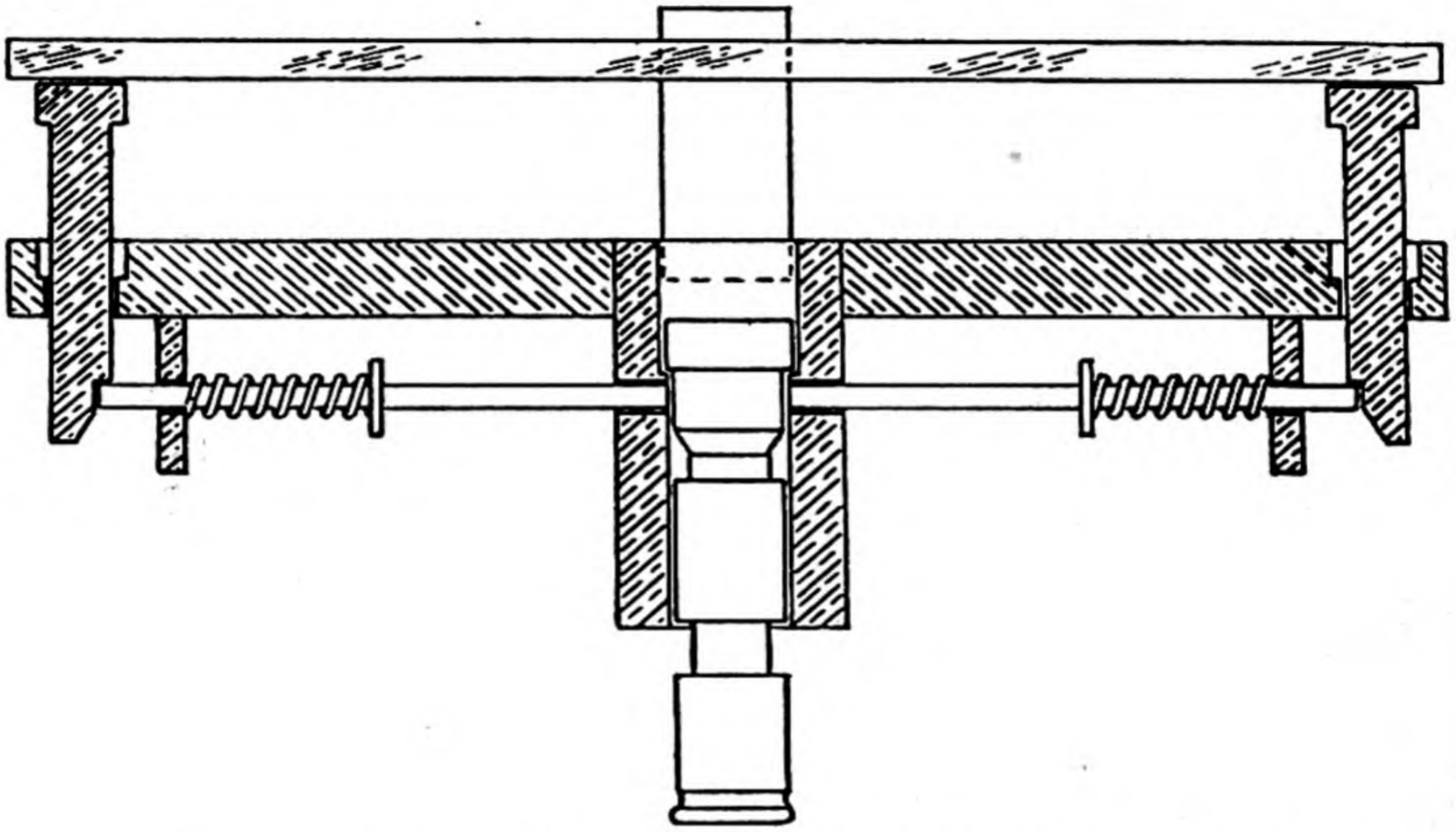


Figure IV-4. Spreadometer for control of ink flow.

CHAPTER V

FLOW OF INK ON THE PRESS

A. INTRODUCTION

The rheological demands for a satisfactory typographic printing ink follow an exceedingly complex pattern. An analysis of the various stages of the typographic printing process reveals three distinct phases, each having a different rheological ink requirement.[1]

The ink transport toward the press distribution system may be considered as the initial phase. The second phase is the actual ink distribution on the press rollers, culminating in the inking of the plate. The final phase is the ink transfer from plate to paper. The interaction of ink and paper after the impression is considered separately in Part II.

A schematic drawing of a rotary typographic press is shown in Figure V–1. The ink is pumped from tank *A* by pump *B*, through the feeding line *C*, and into the ink fountain *D* of the press. This forms the ink transport phase. Inks of a heavy consistency, such as those required for the slower presses, are not pumped, but are fed directly from the containers into the ink fountain *D*.

The ink distribution mechanism starts where the fountain roller *E* takes up the ink and carries it into the next series of steel rollers *S* and rubber rollers *R*, until it is finally distributed as a film on the plate fastened to the plate cylinder *P* of the rotary press. In a flat-bed press basically the same process is followed, but a flat form is used instead of a cylindrical plate.

The ink transfer mechanism is the final phase. It represents the stage in which the ink is transferred from ink to paper and the form is separated from the print. In Figure V–1 the inked plate cylinder *P* is pressed against the paper web *W*, which is held in place by the impression cylinder *I*.

B. TRANSPORT PHASE

Discussing the rheological requirements for a printing ink in the various phases, we notice that the object of the transport phase

[1] A. Voet in *Proceedings of the International Congress on Rheology*, North Holland, Amsterdam, and Interscience, New York, 1948, p. II–252.

is to bring the ink into contact with the fountain roller in order to feed the ink distribution mechanism. The ink is pumped into the fountain or brought in by other means. In the fountain, which is more or less an open container, the ink is not subjected to shearing stresses, except in the immediate vicinity of the slowly rotating roller. The ink must flow continuously toward the fountain roller to replace ink carried away by the distribution system.

It is therefore clear that in the initial phase the ink must level out by gravity alone without any shearing stresses being applied. This requires a low yield value and the absence of thixotropy. Thixotropy in an ink which is being transported by a pipe line from a tank

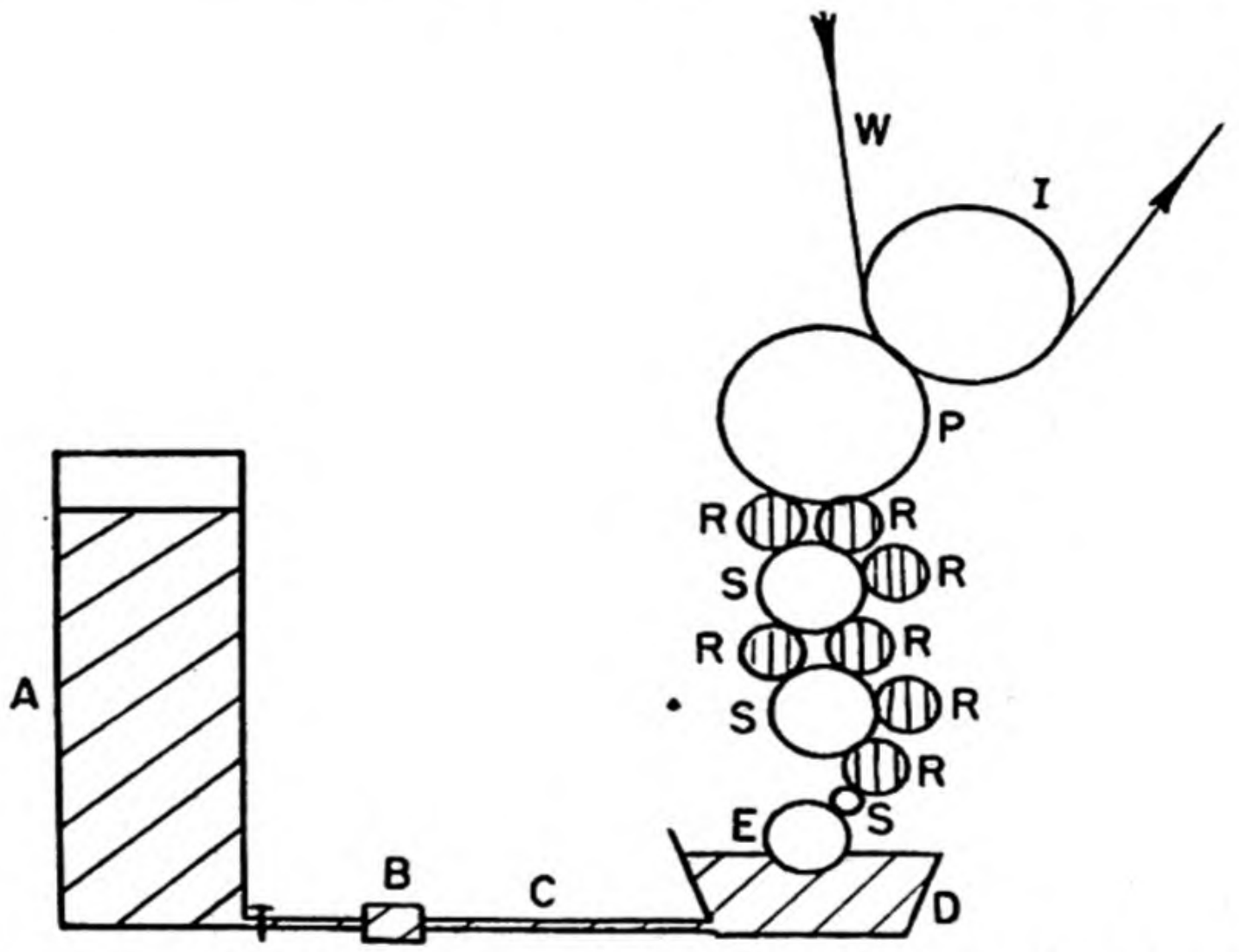


Figure V-1. Schematic representation of the flow of ink on a typographic rotary press.

is entirely unsatisfactory, since it would cause the lines to clog after a prolonged period of rest. Similarly, in the Hoe pump box distribution system, where ink is not fed from an open fountain but is sprayed on the fountain roller by means of a series of fine tubes, a low ink yield value and the absence of thixotropy are required.

C. DISTRIBUTION PHASE

In the distribution phase ink is transferred from steel rollers to rubber rollers and vice versa until finally an ink film is deposited on the form.

On the roller system of the press the ink is discontinuously

sheared. Longitudinal shear, caused by the so-called roller vibration, is also present. The shearing stresses to which the ink on the rollers is subjected are very high. An estimation of the tremendous energy used in shearing the ink between the rollers may be made by means of the inkometer, discussed in the next chapter. This instrument measures the frictional forces exerted by a steel roller upon a rubber roller covered with ink, while speed and ink film thickness are adjusted to actual press speeds.

Calculations on the basis of inkometer data showed that in addition to the deformation energy of the plastic roller, in each transfer phase from one roller to the next in an ink of a viscosity of 174 poises, every cubic centimeter of ink absorbed 2.6×10^9 ergs per second of energy.

One part of this energy is used to split the ink film; another part is used to break up ink particle structures, an important function of the distribution system. A large part of the energy is, without doubt, dissipated as heat.

Accurate estimations of the shearing stress to which the ink is subjected are difficult to make, but at roller speeds of 400 r.p.m., the value of 10^7 dynes per cm.^{2} may not be too far off. Such high shearing stresses of a sufficient duration will completely break up the ink particle structures. We must, however, take into consideration that the shearing is markedly discontinuous. Since the contact area probably does not exceed 5 per cent of the total area, the ink is sheared for a period not exceeding one-twentieth of the total period. In the intermediate periods there is, thus, an opportunity for the partial rebuilding of structures, but experience has shown that with satisfactory inks no substantial rebuilding of particle structure is possible in the fraction of a second. Inks which do show such a quick rebuilding of particle structures are characterized by a high yield value and are therefore unsatisfactory.

The ink must thoroughly wet metal as well as rubber to distribute well. Failure to wet the rollers completely will cause improper distribution. In addition, the ink must transfer properly to each consecutive roller, which occurs only if the ink film during each transfer splits into films of approximately equal thickness, amounting to a 50 per cent transfer. If the ink viscosity is too high for the speed of rotation, ink transfer does not occur properly, and less and less ink is

transferred to each consecutive roller, resulting in a poor inking of the form. During the distribution stage there is then a definite upper limit of allowable ink viscosity for each speed.

Another interesting rheological requirement may be noticed during the distribution phase. Ink transfer from roller to roller occurs through film splitting. Ink films, in the distribution phase, are drawn out in long threads which finally break. As a result of this rupture, and also on account of friction between the rotating press rollers and the paper web, substantial electric charges are generated by a printing press. Therefore during breaking of the ink filaments a rapid disintegration of the ink droplets into fine electrically charged mist particles may follow, owing to the mutual repulsion of the ink particles in the charged droplets.

Ink misting is extremely annoying. It results in the formation of ink deposits throughout the pressroom and is a very serious problem in high-speed printing. Since no practical way has been found to remove static electricity, it is desirable to have inks which do not show a pronounced tendency to mist. Inks with a high pigment loading usually resist misting more effectively than inks with a lower degree of loading. The latter inks, however, are much more fluid than the former.

Consequently our requirements are conflicting. In the transport phase there is an upper limit of viscosity required for the proper distribution of the ink at higher press speeds. This limit appears to be far lower than desirable to reduce misting of inks by higher pigment loading. Thus ink misting is often prevalent in high-speed printing.

D. INK TRANSFER PHASE

In the ink transfer phase from form to paper an interesting and complex series of rheological demands have to be made upon the ink.

The major object of the printing process is to make a reproduction which resembles the original as closely as possible. In halftone reproductions each screen dot has to be reproduced exactly from the original plate in order to form a perfect image. In high-speed typography the ink dot is pressed on the paper at a pressure of about 60 kg. per cm.^{2} for a few milliseconds. Under this pressure, part of the ink may be forced sideways from the center of the protruding dot toward the periphery, thus causing dot distortion in which the center

of a reproduced dot is relatively free from ink, while a large ink agglomeration is found in the periphery. Ink may even be deposited outside of the original dot area.

In letterpress printing a small ink displacement is not always wholly undesirable. However, irregular dot contours are frequently formed, especially when printing on rough papers. To prevent dot distortion and poor reproduction it is imperative to have an ink of high resistance to deformation, requiring a high viscosity.

Since the ink displacement to the dot periphery results from a very high shear, inks should be resistant to deformation while subjected to high shear.

The process of ink transfer, however, is only finished after the form has been separated from the paper, making film splitting necessary. As a result of the ink film splitting the forces exerted upon the paper are considerable. They are caused by the resistance of the ink to separation, which is known as tackiness or tack. If the resistance to separation of an ink is sufficiently great, the paper is completely ruptured, a phenomenon known as picking. It is obvious that to avoid picking, inks must not be too tacky, but unfortunately, tack is a property related to viscosity and the more viscous inks usually are also the tackiest. Consequently, in the phase of ink transfer from form to paper, the ink must have as high a resistance to deformation as is compatible with the tackiness permitted by the web speed and by the resistance to picking of the paper.

The forces exerted by the separating surfaces increase as the rate of separation increases and the tack of inks increases with speed. In other words, the slower the press, the less is the ink tack. In accordance with the desire for the best reproduction slow press speeds will permit the use of more viscous inks. Since the same requirement is valid in the distribution phase, the rule in typographic printing is that the slower the press, the more viscous should be the ink used.

Unsatisfactory rheological characteristics of typographic printing inks may result in filling in of the halftone screens. This phenomenon is especially marked with inks in which the structure builds up very rapidly after discontinuation of the shearing stress. Inks of this type are plastic, with a very high yield value and a pronounced thixotropy. The filling in of the plates is caused by the failure of the ink to transfer properly from plate to paper owing to particle struc-

tures formed in the absence of shear during the short period of time between the inking of the plate and the impression. By adding excess of beeswax to an ink which performed satisfactorily before, it was shown that the yield value was markedly increased and fill-in of screens was induced.[2]

[2] D. Tollenaar in *Proceedings of the International Congress on Rheology*, North Holland, Amsterdam, and Interscience, New York, 1948, p. II–261.

CHAPTER VI

SEPARATION OF INK FILMS

A. INTRODUCTION

The final move in the transfer phase on a printing press is usually the separation of the inked plate and the paper after the impression. The resistance which is offered by the ink film subjected to stresses and which causes film splitting is known as tack. Tack plays a very important part in the properties of inks, for distribution, transfer, and quality of the printed reproduction are directly related to the tack of the ink.

Many attempts have been made to evaluate the tack of inks. Since time immemorial craftsmen have used the finger tap-out test, by which the finger tip is pressed on an inked surface and drawn away suddenly. The action is repeated a number of times in rapid succession, and the tack of the ink is estimated from the amount of pull resistance experienced. This simple and easily performed test inevitably has many defects. First, the human element, an uncertain one, plays a major part: the estimate of pull resistance and the comparison with a standard is very uncertain; the rate of successive finger motions and the pressure exerted by the finger are important factors which cannot be duplicated accurately by different operators and not even exactly maintained by the same operator. Secondly, the tap-out test does not allow a numerical evaluation. Thirdly, the most important basic objection to a finger tap-out test, either by a human finger or by a mechanism imitating the test, is that the test does not duplicate the actual manifestation of tack on a press. Neither the state of agitation of the ink nor the film thickness or rate of film separation actually approaches those existing on a press during actual printing operations. The peculiar character of the phenomenon of film separation seems to make it a prerequisite to obtaining significant results that press conditions be reproduced more or less accurately during the measurement. It is thus understandable that many attempts to measure the tack of inks have been reported in the literature.

B. MEASUREMENT OF TACK FORCE

1. Stefan's Fundamental Work

The earliest work on tack was carried out by Stefan,[1] who studied the problem theoretically as well as experimentally to determine the forces involved in the process of separating two parallel plates immersed in a viscous liquid. Stefan's results may be expressed by the following equation:

$$F = 3\eta O / 4th^2 \qquad (28)$$

indicating that the force F necessary to separate the plates is proportional to the viscosity of the liquid η and to the area of the plate O and inversely proportional to the square of the distance of the plates h and the time of separation t. Actually Stefan's system may be considered as a parallel plate viscometer with plates moving away instead of approaching. Stefan's theoretical results were later generalized by Reynolds.[2]

Experimentally Stefan's equation is justified, provided a small correction is made which takes into account the surface roughness of the plates. Stefan's equation describes the resistance to separation of two surfaces separated by a viscous liquid satisfactorily for a slow separation by liquid flow. It is of interest to notice that the force required for separation is larger for thinner films. This is easily understood since the separation occurs by liquid flow in the capillary spaces between the plates. The smaller the space, the more pronounced the resistance to flow.

2. Bekk Viscometer

Bekk[3] observed the motion of a steel hemisphere through a film of printing ink deposited in a recession of a steel plate. His viscometer, provided with a long lever arm and a microscopic reading device is illustrated in Figure VI–1. The instrument permits an accurate estimation of the force necessary to make the hemisphere travel through a thin film of ink in a predetermined period of time. As an example, the force may be established to traverse a film with a thickness of 10 microns in 3 seconds.

Bekk measured both the resistance to a downward motion of the

[1] J. Stefan, *Sitz. Kais. Akad. Wien, Math. Nat. Kl., A69,* 713 (1874).
[2] O. Reynolds, *Phil. Trans. Roy. Soc. (London), 177,* 157 (1886).
[3] J. Bekk, *Deut. Drucker, 44* (256), 450 (1938).

hemisphere, described as "push resistance," as well as the resistance to an upward motion, identified as "pull resistance" or tack. Bekk's viscometer differs from conventional viscometers basically in that the measurements are carried out in thin ink films.

The viscosity of films approaching molecular dimensions may differ considerably from the viscosity in bulk. It is equally true that the viscosity of films of orientated molecules may not be the same as the viscosity of randomly distributed molecules. There is, however, no physical reason why the films used in the Bekk viscometer, of a thickness of 10–50 microns, should have a viscosity different from the viscosity in bulk.

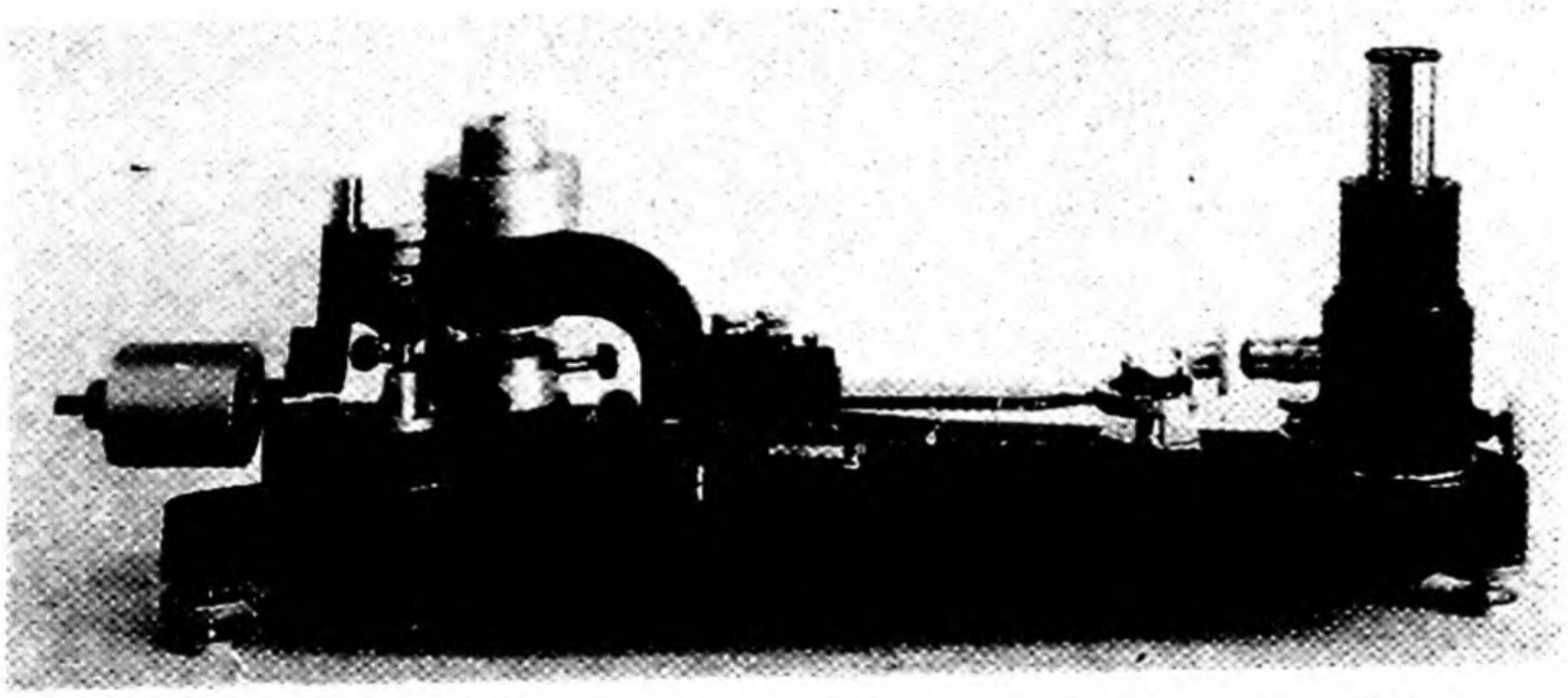


Figure VI-1. Viscometer for inks according to Bekk.

Bekk's viscometer does not solve the major problems of state of agitation and rate of separation of ink films, since neither quantity ever approaches those prevailing on a press.

3. Green Tackmeter

An instrument known as the "tackmeter," developed by Green,[4] was constructed to operate essentially as a mechanical finger. The instrument imitates finger tap-out tests, but allows a numerical evaluation of the pull resistance encountered at a controlled, constant temperature. Various sizes of mechanical finger tips as well as different film thicknesses may be used.

The rate of film separation in the instrument, however, is of a much smaller order of magnitude than the rate of film separation encountered on a press. As a result Green's instrument acts very much like Stefan's parallel plates, and the quantitative results are

[4] H. Green, *Ind. Eng. Chem., Anal. Ed., 13,* 632 (1941).

identical. Thus, the Green tackmeter is basically a parallel plate viscometer in which the plates are moving away instead of being made to approach each other under the influence of a force. It is therefore a rather indirect way of measuring the viscosity of a Newtonian liquid. For a non-Newtonian liquid the same difficulties are encountered as in a capillary viscometer, since plug flow cannot be eliminated completely. The Green tackmeter, therefore, is not a suitable instrument to evaluate the tack of inks.

4. The Inkometer

The inkometer, developed by Reed,[5] was designed to measure the tack of inks under dynamic conditions closely resembling those existing on a printing press.

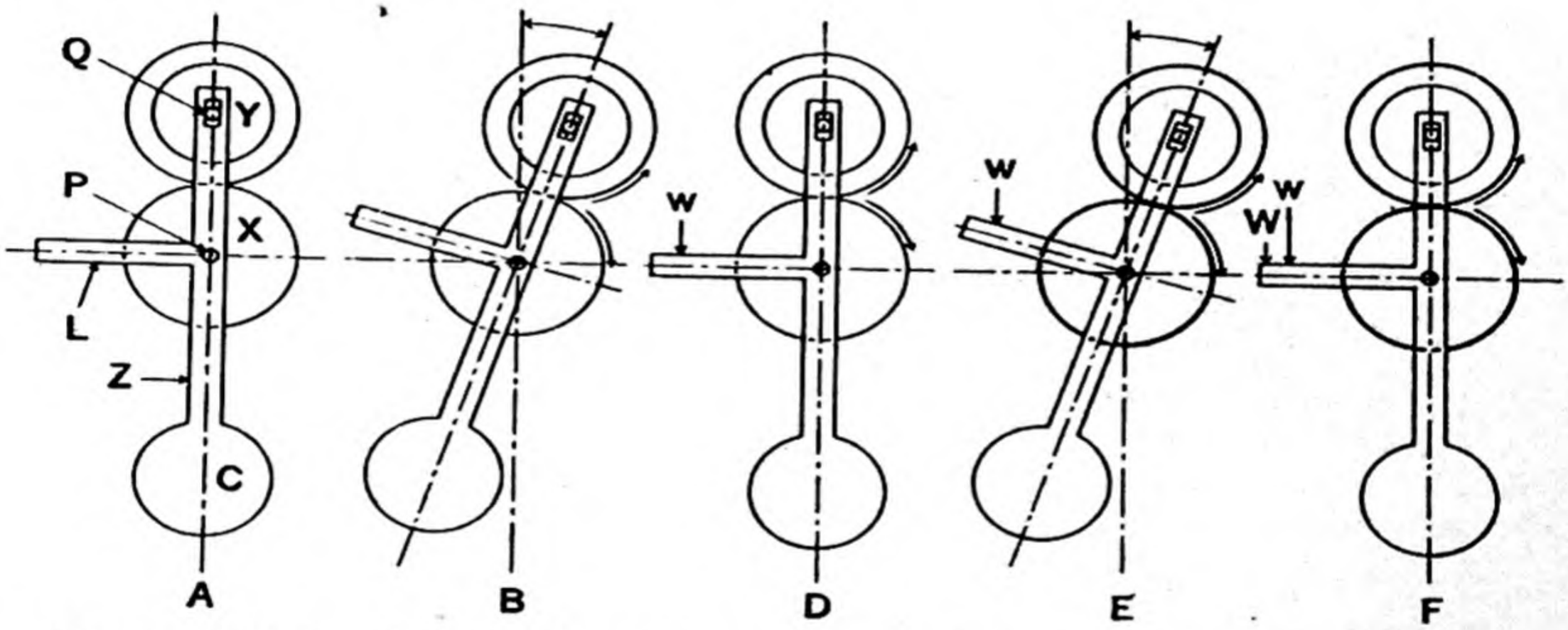


Figure VI-2. Schematic representation of the inkometer principle.[5]

The instrument is essentially an ink film dynamometer. It measures the force required to cause two inked rollers *X* and *Y* to rotate in contact with one another at a predetermined pressure, speed, and temperature. The rubber roller *Y* rotates around shaft *Q*, while the metal roller *X* is driven by shaft *P*. The swinging frame *Z* has an arm *L* and a counterweight *C*.

Figure VI–2A shows the swinging frame in static balance with the rollers free from ink and at rest. Figure VI–2B shows the angular displacement of the swinging frame *Z* resulting from rotating the roller *X* by frictional forces, in the absence of ink. Figure VI–2D shows the balance restored by application of the force *w*. Figure

[5] R. F. Reed, *Am. Ink Maker, 16,* (2), 37 (1938).

VI–2E indicates the angular displacement of the swinging frame Z when ink is applied to the rollers after they have first been balanced. Finally, Figure VI–2F shows the balance again restored by the application of the force W, the moment of which equals the torque produced by the ink film.

During the rotation of the rollers two ink films unite into a single film, which is then subjected to shear between the metal and rubber roller. Finally, the film is split again. The total moment of the forces involved is equal to the torque produced by the ink and is classified by Reed as tack.

The inkometer may be used at speeds equal to actual press speeds, thus producing rates of film separation of the same magnitude as rates of separation encountered on a press.

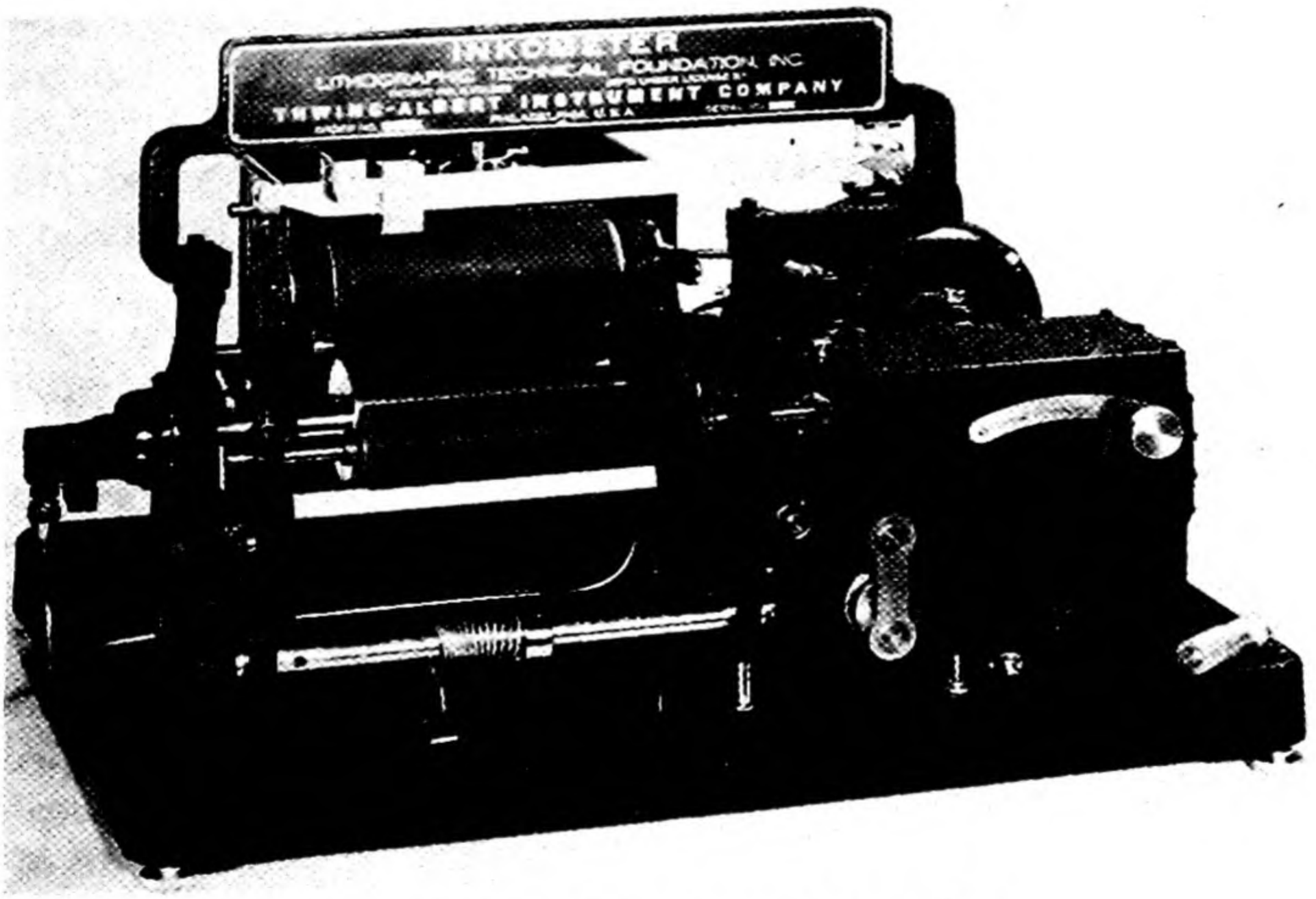


Figure VI-3. Inkometer, front view.

The temperature of the ink is controlled by forcing water of a thermostatically controlled constant temperature bath to circulate through the hollow metal roller. A frontal view of the inkometer is reproduced in Figure VI–3.

The inkometer appears to approach the conditions existing on a printing press much more closely than any other instrument proposed.

It may even be mounted on a printing press and operated as an integral part of the press.[6] It has found extensive application in practical ink testing.

One of the important uses of the inkometer is to predict ink trapping in wet multicolor printing. To print satisfactorily, each consecutive colored ink must be deposited in a smooth film on the surface of the previous ink film, a procedure called trapping. Improperly trapping films do not lie smoothly and may even pull off parts of the previously printed film, as will be more fully discussed in a later chapter. The condition for proper trapping is that each film must have a more pronounced resistance to film separation, or tack, than the film immediately preceding it.

Since tack depends on the rate of film separation, it is imperative to measure the tack for each ink at the proper press speed, especially since inks which trap satisfactorily at low speeds do not necessarily do so at high speeds. The inkometer will register the torque due to ink tack at any desired press speed, making it possible to adjust the inks used in wet multicolor printing to the desired tack ratio at the actual press speed.

The inkometer has also found extensive use in the control of heatset inks. Heatset inks are based on higher boiling solvents which evaporate only slowly at room temperatures but rapidly at the temperature of drying oven or steam drum used for solvent evaporation required with heatset printing presses. A solvent which evaporates too rapidly at room temperatures will cause excess tack in an ink during printing, resulting in improper ink transfer and possibly in rupture of the paper surface (picking). On the other hand, inks which evaporate too slowly will require excessive heat to dry properly, which is not only uneconomical but also leads to a serious weakening of the paper and causes frequent web breaks. A proper rate of evaporation is therefore an essential property for a heatset ink.

The desirable rate of evaporation is closely connected with press speed. Not only is the time required for the transportation of the ink inversely proportional to the press speed, but also faster moving and more rapidly separated ink films in contact with air show an increased rate of evaporation. The inkometer registers the change of tack with time for a given heatset ink by solvent evaporation at a given press speed at a controlled temperature. The allowable in-

[6] C. C. Mill, E. R. Gates, and L. E. Lawson, private communication.

crease of tack with time may be recorded by means of inks which perform satisfactorily on the press. A desirable range for the change of tack with time may then be established empirically. Inks which show a proper change of tack with time should then be satisfactory from the standpoint of rate of evaporation and press stability.

It must be remarked that such empirical relations are valid only for inks of a basically similar composition. Thus, such a method will be satisfactory for inks based on petroleum hydrocarbons which have similar resinous binders, but it does not necessarily follow that the same relationship holds also for aqueous or alcoholic vehicles or for completely different synthetic resins. Identical inkometer data could possibly result in unsatisfactory press behavior where such differences in composition exist. Care should therefore be taken in applying inkometer data to heatset inks not to exceed the limit of applicability of the empirical relations requiring chemically similar solvents and binders.

The inkometer is an important control instrument, but its usefulness as an instrument of more fundamental research is a different matter. A most important objection to its use in fundamental investigations is the inability of obtaining data in fundamental units. Although the torque is measured in gram-meters, it is impossible to indicate the tack in c.g.s. units independent of instrumental constants. The indirect approach by standardizing inkometer torques by means of a Newtonian liquid of known viscosity fails equally. Liquids of low viscosity do not distribute properly on the rollers. Liquids of higher viscosity are drawn out in filaments and are eliminated from the rollers by a process known as "misting," discussed more fully later in this chapter. Thus, inkometer data are necessarily dependent upon the dimensions and construction of the instrument and have no independent significance. This fact seriously hampers a more fundamental consideration of inkometer data.

Another point is the influence of the deformation of the composition or rubber rollers and its effect on inkometer data. It appears that the simple method used for balancing the inkometer is not entirely satisfactory. The balancing weight is not independent of the speed, and the beam must generally be balanced for every speed used. This phenomenon is very marked with synthetic rubber rollers, indicating the influence of a nonideal elastic behavior. This is also indicated by the marked rise in temperature within the rollers and not

on the surface alone. As a result considerable energy is expended on deformation of imperfectly elastic rollers. This energy is actually measured as ink tack. The serious lack of agreement between data obtained with the aid of different inkometers is caused by this undesirable roller effect.

Another observation is that the distance between the rollers is not constant, but varies with the speed as a result of the variation of roller deformation. King[7] modified an inkometer by maintaining a constant distance between the rollers, resulting in a constant roller deformation independent of the speed. The data obtained showed a linear plot of torque against speed with a positive intercept common to all materials, a result not found with a standard inkometer.

From the above it appears that inkometer data include various factors not connected with the tack of inks. These factors are dependent upon the roller speed and are not eliminated by the balancing system. They are, in addition, not independent of the design and dimensions of the instrument. It is therefore not surprising that the inkometer, notwithstanding its widespread and successful practical use over a number of years, has contributed little to a more fundamental understanding of the phenomenon of tack.

A redesign of the inkometer to eliminate at least some of the fundamental objections does not appear to be impossible, but the fact that in its present form the instrument is satisfactory for practical control makes a basic change in the commercially available inkometers rather remote.

C. TACK AS A VISCOELASTIC STRESS RELATION

1. Mechanism of Tack

When subjected to stress the response of the ink, and of any liquid, may be of a viscous and of an elastic nature. Splitting of ink films will occur by viscous flow when the rate of separation is slow. The liquid ink will respond to the stress by viscous flow, since the time element involved is long enough to allow flow to take place. Upon increasing the rate of film separation, however, the flow response to stress of the liquid, being proportional to the elapsed time, will become less and less pronounced. On the other hand, the elastic response, of an instantaneous nature, becomes more and more important. We may thus expect that with a given, critical, high

[7] C. King, *Am. Ink Maker, 28* (4), 31 (1950).

rate of film separation the ink, though a plastic liquid, actually has more of the behavior of an elastic solid. Rupture will then occur when the applied force exceeds the cohesive material strength.

From a visual examination of the ink flow on rotating rollers it appears that film splitting is preceded by the formation of thin ink filaments which are elongated and finally break. The higher the rate of film separation, the shorter the ink filaments are at the rupturing point.

The formation and splitting of ink filaments on rotating rollers has been examined by Sjodahl.[8] From photomicrographs taken with

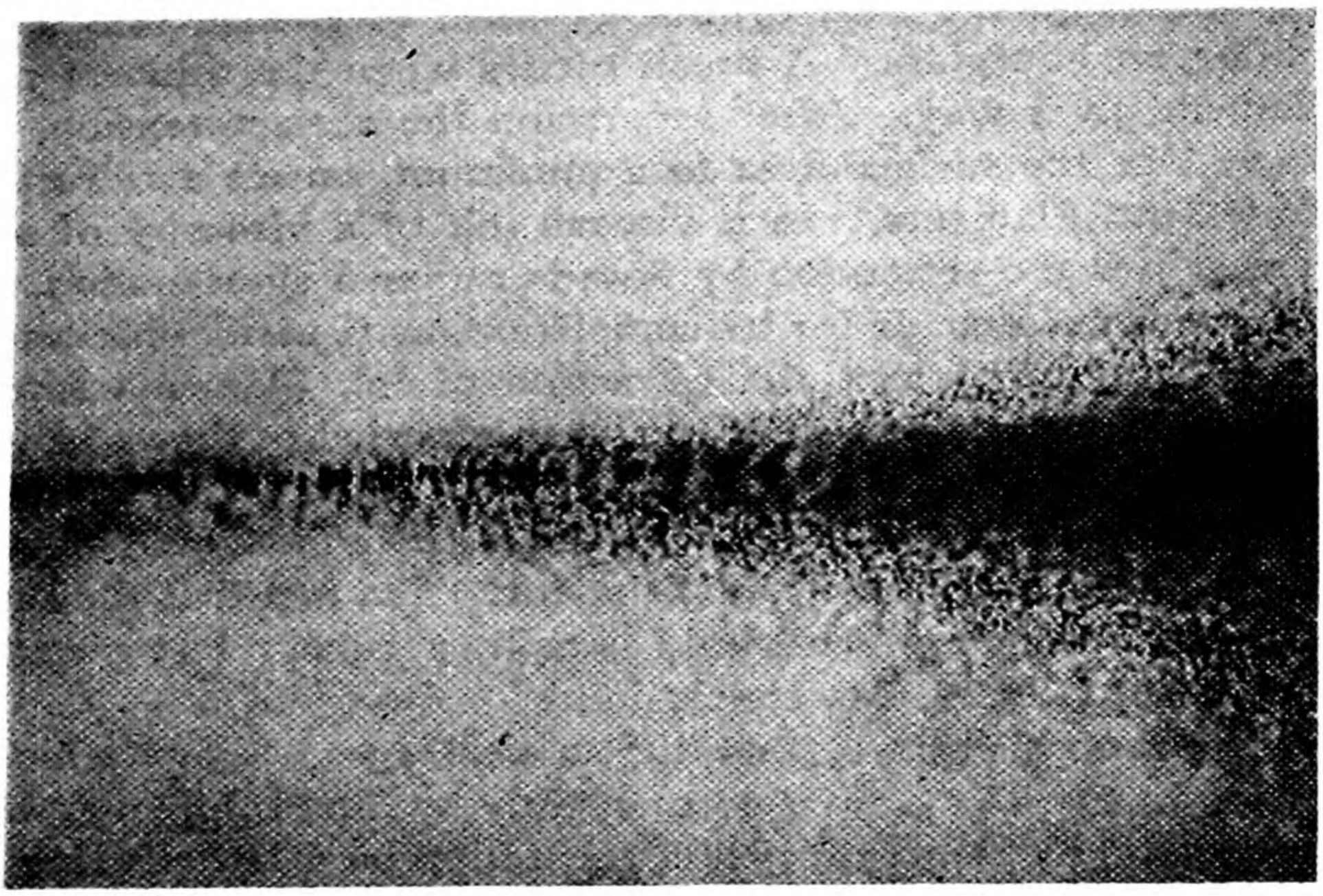


Figure VI-4. Photomicrograph of rotating inked rollers at an exposure time of 2×10^{-6} second.[8]

the aid of a microflash in an exposure time of two-millionths of a second it was observed that for viscous inks at high speeds the ink filaments reached an elongation of several times the original film thickness before a break occurred.

Figure VI–4, taken in the direction of the axis of the rotating rollers, shows filamentation at an enlargement of 6.4 × for a white offset ink at a peripheral roller speed of 900 ft. per minute.

It is remarkable that immediately after rupture hardly any

[8] L. H. Sjodahl, *Am. Ink Maker, 29* (3), 31 (1951).

broken filaments remain visible. At the exceedingly small exposure time, permitting the close examination of phenomena occurring in a period of time of 10^{-6} up to 10^{-3} second after the break, the intermediate stage of partly receding filaments is visible for a period of time of less than 10^{-5} second on the photomicrograph. This indicates that film separation is counteracted by extremely powerful elastic forces acting in the liquid.

If an ink filament is drawn out slowly, its deformation occurs by liquid flow. The diameter of a filament is gradually reduced in the middle parts by process of slow elongation ("necking down"), causing the originally near-cylindrical form to change into a shape resembling an hourglass. A break occurs when the thinnest part of the filament gives way. After separation the surface tension, which acts to reduce the surface area to a minimum, causes a retraction of the drawn-out filaments. In a viscous ink of a viscosity of several hundred poises the retraction by flow is rather a slow motion, which may take several seconds for its completion, as is easily observed.

The observation that the retraction of ink filaments separated at high speed in the viscous ink occurs in a period of time of an order of probably one- to ten-millionths of a second is an indication that film separation in this case does not occur by liquid flow but by rupture of a material with an elastic behavior. The fact that the shape of the filaments remains cylindrical, as with a rubber test piece being expanded, emphasizes this conclusion.

It appears, therefore, that the critical speed above which film separation in the inks cannot occur mainly by liquid flow may be well within the range of the rate of film separation on a fast printing press. The mechanism of rapid film separation may therefore follow the pattern of a solid rupture, a point which will be more fully elucidated later.

2. Tack Energy

A quantity of fundamental importance is the tack energy. This quantity denotes the total energy necessary to cause film separation.

In a process of solid rupture we must distinguish between different types of solids. A brittle solid is characterized by pure elasticity. For such a brittle material the maximum energy necessary to cause rupture is equal to the energy required to form the new surface, although the presence of structural flaws usually reduces this quantity

materially. The free surface energy has a value of not more than a few hundred ergs per square centimeter for most solids. The maximum rupture stress may be indicated by dividing the free surface energy by the distance over which the attractive forces operate.

In systems consisting of large, highly elongated molecules more complicated reactions to mechanical stress may occur. Such responses reveal not only the characteristics of the individual long chain molecules but also the interactions with neighboring chains.

We must, in addition, distinguish between two different ways of applying a load to a material, namely, the static and the impact methods. Static loads are applied slowly and are increased until their maximum value has been attained, which is followed by failure of the material. The stress necessary to cause failure is the tensile strength of the material.

Impact loads are applied suddenly, or with shock. Their effect is usually much more pronounced than the effect of an equal load applied slowly. In addition, impact loads induce vibrations. Stresses and strains may even be propagated as shock waves at very high rates of deformation.

The essential ultimate property in an impact test is not the maximum stress supported by the sample, but rather the energy necessary to cause failure. The deformation of an ink film in the process of film separation is not caused by a slowly increasing stress, but is sudden and rapid and thus clearly an impact deformation. It is therefore essential to consider the energy of separation, instead of the maximum stress necessary to cause film break.

The average value of the free surface energy of inks is of the order of 30 to 50 ergs per cm.^{2}. The energy required for rupture, in a solid pattern, may even be reduced as a result of flaws caused by the release of dissolved gases, resulting in filamentation.

Actually, as will be shown later, the energy of separation is of a much higher order of magnitude than the values indicated above. This proves that the greater bulk of the energy required is used in the initial phase of film separation, the elongation of the ink filaments. This process, therefore, is of major importance and has to be considered in full detail in any study of ink tack.[9]

[9] A. Voet and C. F. Geffken, *Ind. Eng. Chem.*, *43*, 1614 (1951).

3. Rolling Cylinder Tackmeter

The rolling cylinder tackmeter embodies most of the requirements set forth previously. It consists essentially of a metal cylinder, which is rolled down an inclined plane, in the pattern of a roller coaster. The metal cylinder *A* (Figure VI–5), with a length of 10.7 cm. and a diameter of 5.25 cm., is electromagnetically released at *B*. The cylinder then rolls down the plane formed by the U-shaped tracks *C* and upwards again, after passing the lowest point. The greatest height reached on the upward swing is now recorded by means of a scale. In a companion test the experiment is repeated, but a small inked metal plate of a length equal to the cylinder circumference is now placed in the path of the cylinder. When the cylinder passes, part of the ink is transferred from the plate to the cylinder, neces-

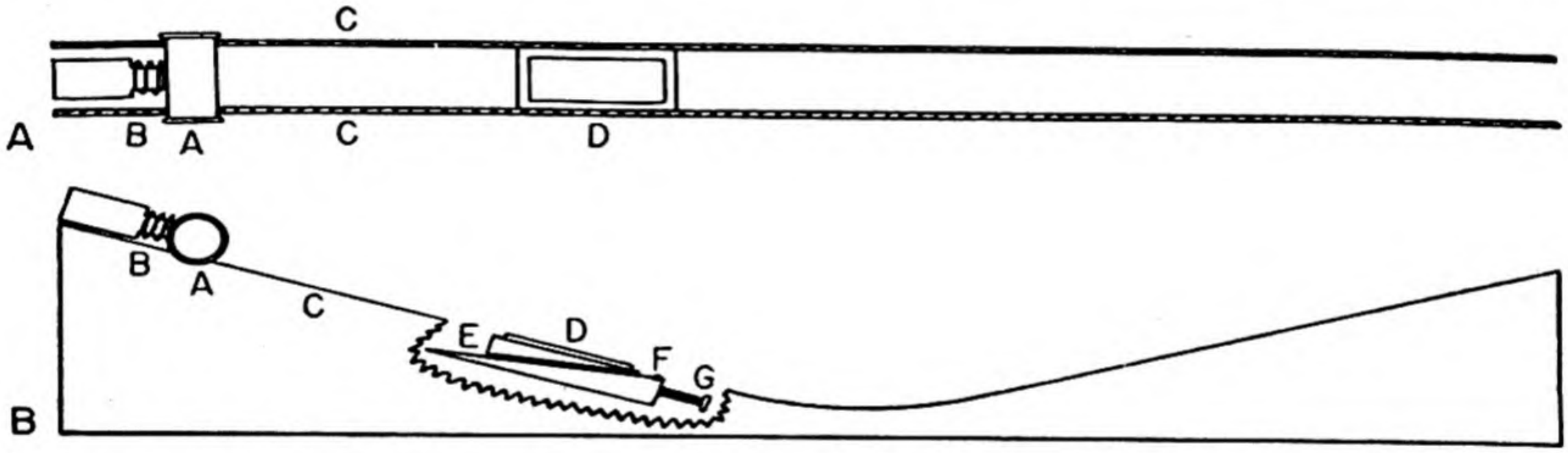


Figure VI-5. Schematic representation of the rolling cylinder tackmeter: (A) top view; (B) side view.

sarily requiring energy. The cylinder now reaches only a lower point on the scale. The difference in potential energy of the cylinder at the end of each of the tests is indicated by the difference in height reached. This energy, corrected for frictional losses, is used for film splitting and may be calculated directly in absolute units.

The cylinder may be covered with papers of different characteristics. The plate *D* may be provided with a film of ink, varnish, oil, or any other liquid or plastic of a desired thickness, by means of a film applicator. The plate may be lifted from the instrument and weighed on an analytical balance, making it possible to measure accurately the quantity of ink applied to the plate and the quantity transferred to the cylinder. Test plates of different surface areas may be used, or a given plate may be partly inked. Rollers of different weights may be used. Different roller speeds are reached by releasing

the rollers at different heights or by modifying the angle of inclination of the plane. Speeds corresponding to medium high printing speeds, up to 500 ft. per minute, are easily reached with the instrument.

A series of experiments were carried out with the object of investigating the influence of the film thickness on the tack energy. When plotting the tack energy against the film thickness in a diagram, irregular curves were obtained for different inks on different surfaces, indicating a complicated relationship. The tack energy, however, appeared to be directly proportional to the thickness of the transferred part of the film, as indicated in Figure VI–6. While the

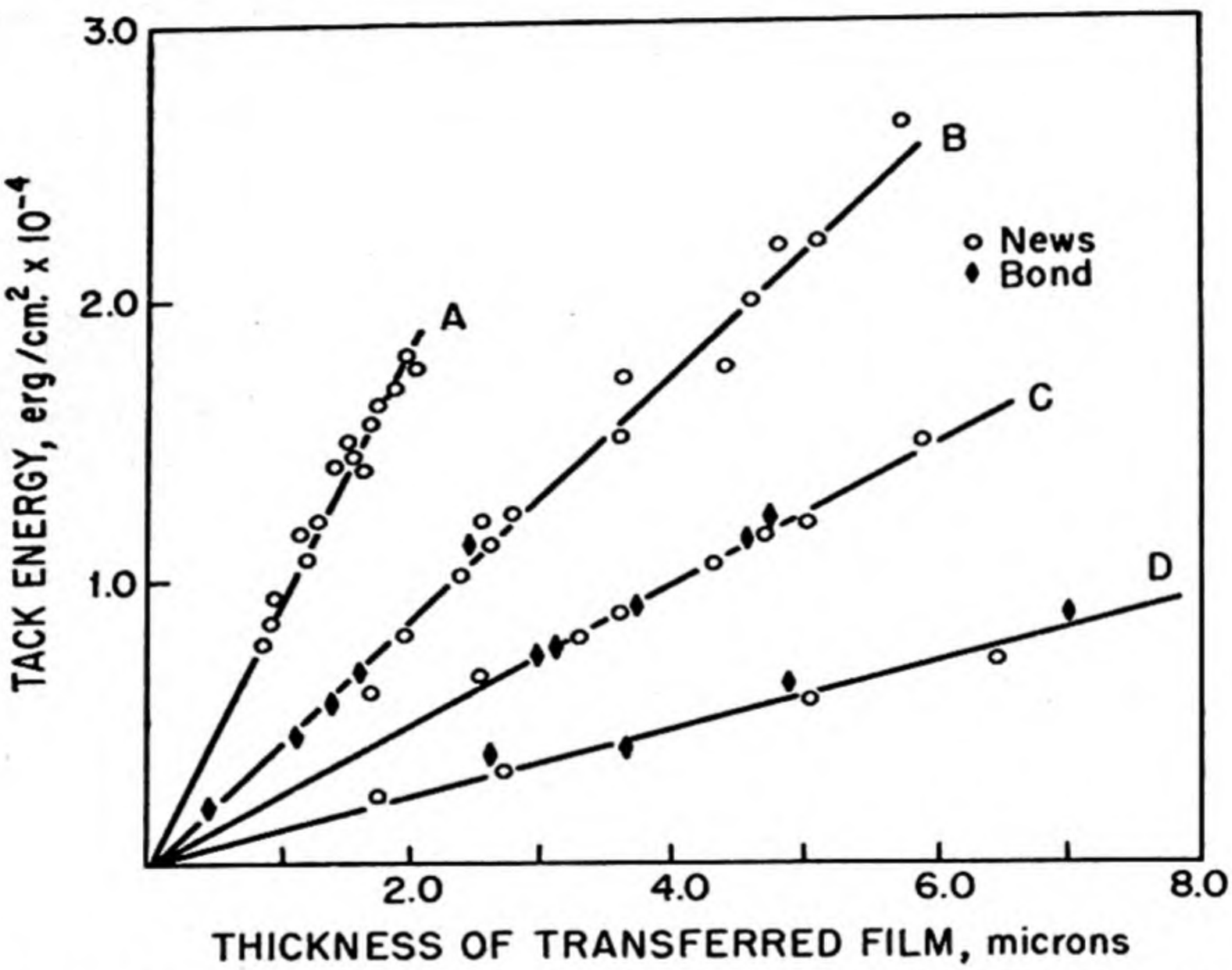


Figure VI-6. Relation between tack energy and transferred film thickness: (A) publication green; (B) rotary blue; (C) magazine black; (D) mineral oil.

tack energy per unit area varies for different surfaces for a given ink, the tack energy density, defined as the tack energy per unit volume of transferred film, is entirely independent of the nature of the surface and is solely determined by the ink. The tack energy for a black ink on different surfaces is indicated in Figure VI–7. The slope of the line is the tack energy density. An important characteristic of the ink, therefore, is its tack energy density at the given rate of separation, of a dimension of $ml^{-1}t^{-2}$. Table VI–1 indicates the tack energy densities for a number of inks at a peripheral roller speed of 235 cm.

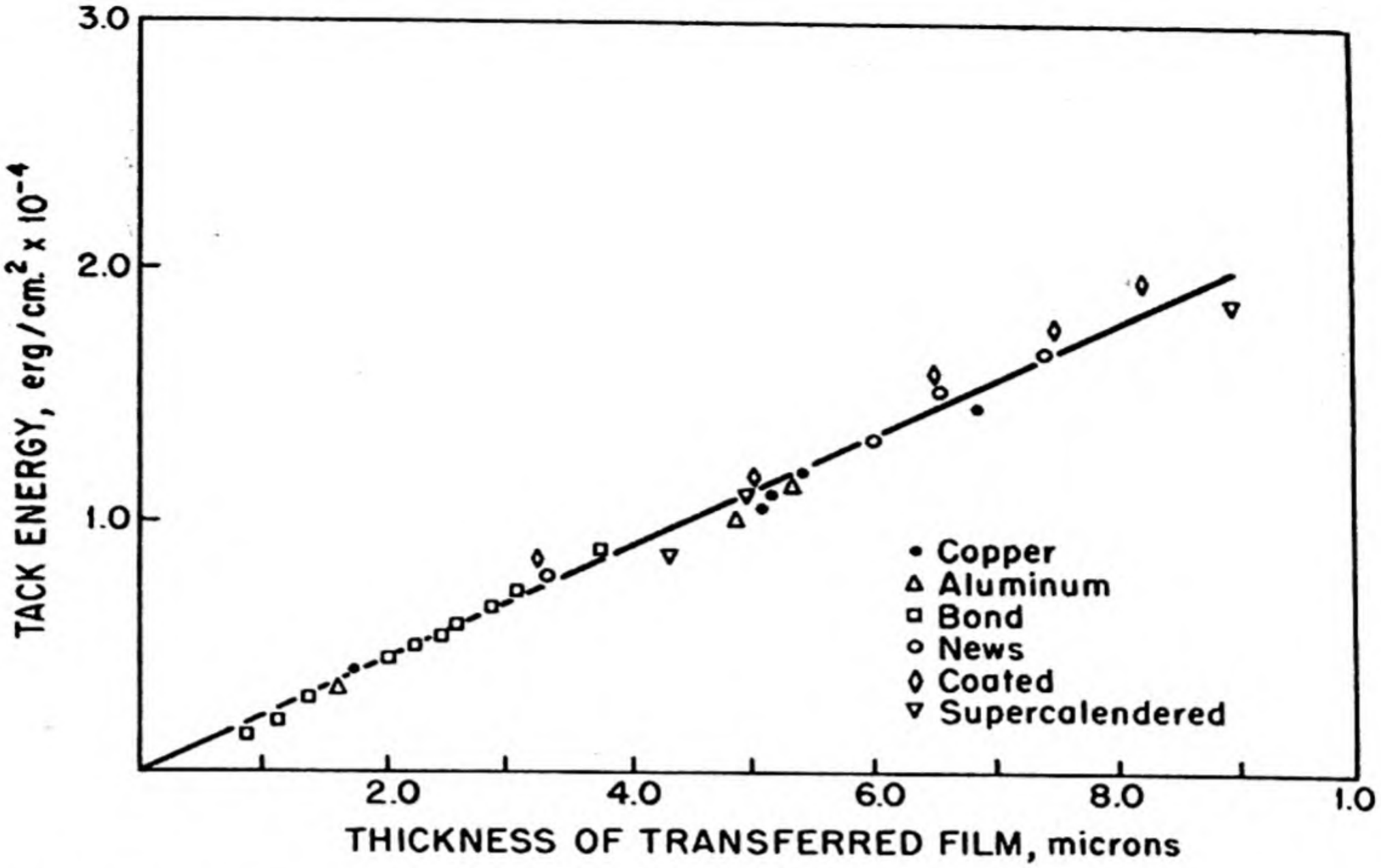


Figure VI-7. Relation between tack energy and transferred film thickness for an ink on different surfaces.

per second. Included are also the plastic viscosity values obtained by means of a rotational viscometer, using the equilibrium method.

Figure VI–8 shows the tack energy density plotted against the viscosity in a logarithmic diagram. A straight line relationship is

TABLE VI–1

Viscosities and Tack Energy Densities

Ink	Plastic viscosity, poises	Tack energy density, D_{23s} in ergs per $cm^3 \times 10^{-7}$	Temp. °C.
News red	25	0.37	24.6
Magazine red	400	30.0	23.3
Mineral oil varnish	220	13.0	23.6
Publication green	210	10.7	23.9
Rotary blue	192	10.2	23.9
Magazine black	77	2.4	22.0
Mineral oil	80	2.5	23.3
Mineral oil	56	1.4	23.4
Rotary red	45	1.1	23.3
Rotary blue	45	1.1	23.3

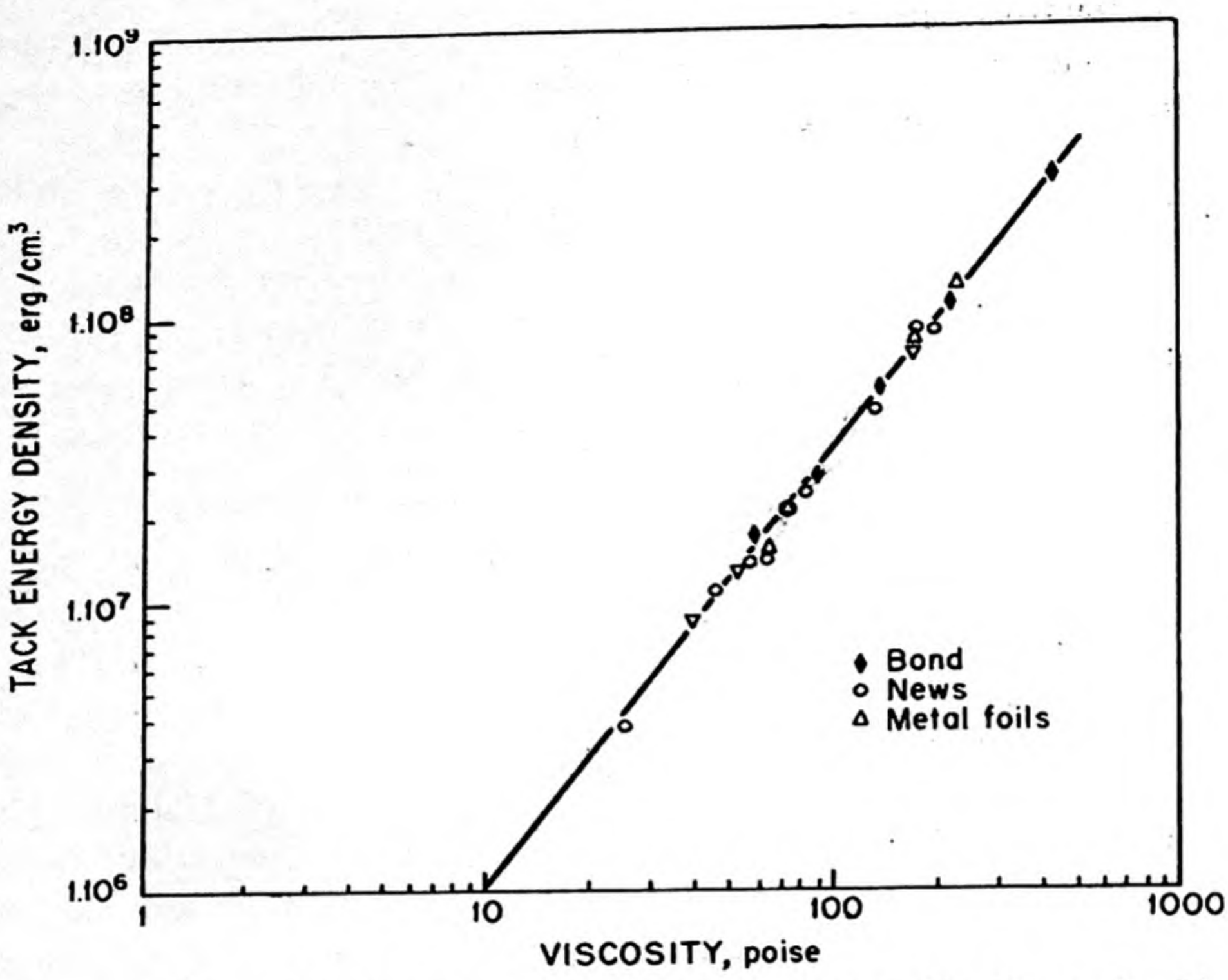


Figure VI-8. Relationship between tack energy density and viscosity for various inks on different surfaces.

found, indicating the validity of the following experimental relationship:

$$D_{235} = K_{235} \times \eta^{3/2} \tag{29}$$

The exponential of the viscosity is derived from the slope of the line in the diagram. The value of K_{235} is 3.35×10^4, as found from the intercept.

Tack energy densities have been measured at different temperatures. The logarithm of the tack energy density is, within the range investigated, from about 10° to 30°C., inversely proportional to the absolute temperature.

A most important factor influencing the tack energy density is the speed of the roller. Extensive experiments showed that the tack energy density is proportional to the roller speed. Combining equation (29) with the proportionality between D_V and V one finds:

$$D_V = K \times V \times \eta^{3/2} \tag{30}$$

The constant K was found to have the numerical value 142. The

equation permits the numerical calculation of the tack energy density from the plastic viscosity at any desired roller speed, corresponding to any desired web speed.

It must be remarked that the pressures applied by the roller are only a fraction, up to 20 per cent, of the pressures applied in the printing process, which are of the order of 750 p.s.i. As a result ink transfer in the rolling cylinder apparatus is only a fraction of the transfer encountered in printing, which leads to marked differences with actual printing (more fully discussed in Part II).

4. Static and Dynamic Stress Reactions

A liquid film reacts to a static stress by flow and when separated in a film under static conditions follows the laws discovered by Stefan. The dynamic reaction to stress differs fundamentally from the static stress reaction. Film separation in the printing process must be considered as a viscoelastic process in which the elastic component usually overshadows the viscous component, following physical laws which differ basically from those followed under static conditions. In simple viscous flow, therefore, the thinnest film shows the highest rate of film separation, whereas the reverse is true in the rolling cylinder apparatus. Likewise, in viscous flow the resistance to film separation is directly proportional to the viscosity of the liquid, whereas in viscoelastic systems such a simple relationship is no longer valid.

It must be recognized that the expressions "static" and "dynamic" have only relative significance. Their more precise meanings may be derived from the viscoelastic theory of liquid behavior developed by Maxwell.[10] This theory is based upon the concept that every liquid reacts to stress with a viscous and an elastic reaction. Such a liquid may be symbolized by a spring in series with a dashpot, as is indicated in Figure VI–9. The spring S symbolizes the instantaneous, reversible elasticity of the liquid with a shear modulus G, while the dashpot represents the time-dependent irreversible liquid flow with a viscosity η. The shear elasticity of such a Maxwell element can be relaxed, as shown by Maxwell, in the relaxation time τ found from the relation:

$$\tau = 2\pi\eta/G \tag{31}$$

If the stress is applied for a period of time much shorter than

[10] J. C. Maxwell, *Phil. Trans. Roy. Soc.* (*London*), *157*, 49 (1867).

the relaxation time, the flow response is negligible and the reaction of the liquid is purely elastic. In the symbolic representation of the Maxwell element of Figure VI–9 it appears that for a stress of very short duration the dashpot does not even begin to move, while the spring reacts instantaneously. If the stress is applied for a period of time much longer than the relaxation time, the viscous response completely dominates the elastic response to stress. In the symbolic representation of Figure VI–9 such a reaction is indicated by a slowly moving dashpot and is the result of a slowly applied stress, without ever extending the spring. If, however, the duration of the stress

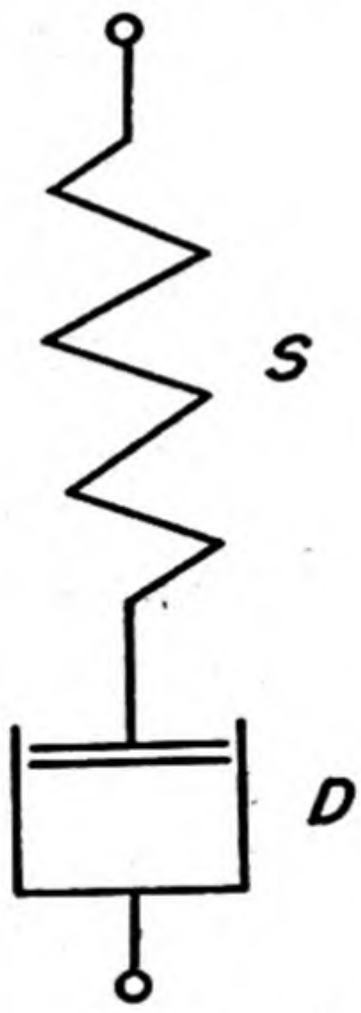


Figure VI-9. Symbolic representation of a viscoelastic Maxwell body.

is of the same order of magnitude as the relaxation time of the liquid, the reaction is of a mixed, truly viscoelastic character.

From the above it appears that a static reaction is a reaction to stress of a duration long as compared to the relaxation time of the liquid, while dynamic reactions are carried out in a time element of the same order or shorter than the relaxation time of the liquid. The exact duration of the relaxation time, therefore, is a significant factor in the phenomenon of film separation. Its calculation is made possible by the relationship (31). The viscosity of inks may be measured directly. The calculation of the relaxation time is only possible if the shear modulus is known.

5. Modulus of Elasticity of Inks

The modulus of elasticity of printing inks may be calculated from the tack energy density by theoretical considerations. It may also be determined directly by experiments.

In order to arrive at an approximated value of the shear modulus for an ink, assume that the duration of the stress impulse is much smaller than the relaxation time of the ink. The flow response is then negligible, and the ink behaves as an elastic solid. Assume further an ideal elastic behavior (Hooke's body) characterized by a linear stress-strain diagram, as indicated in Figure VI–10, in which the

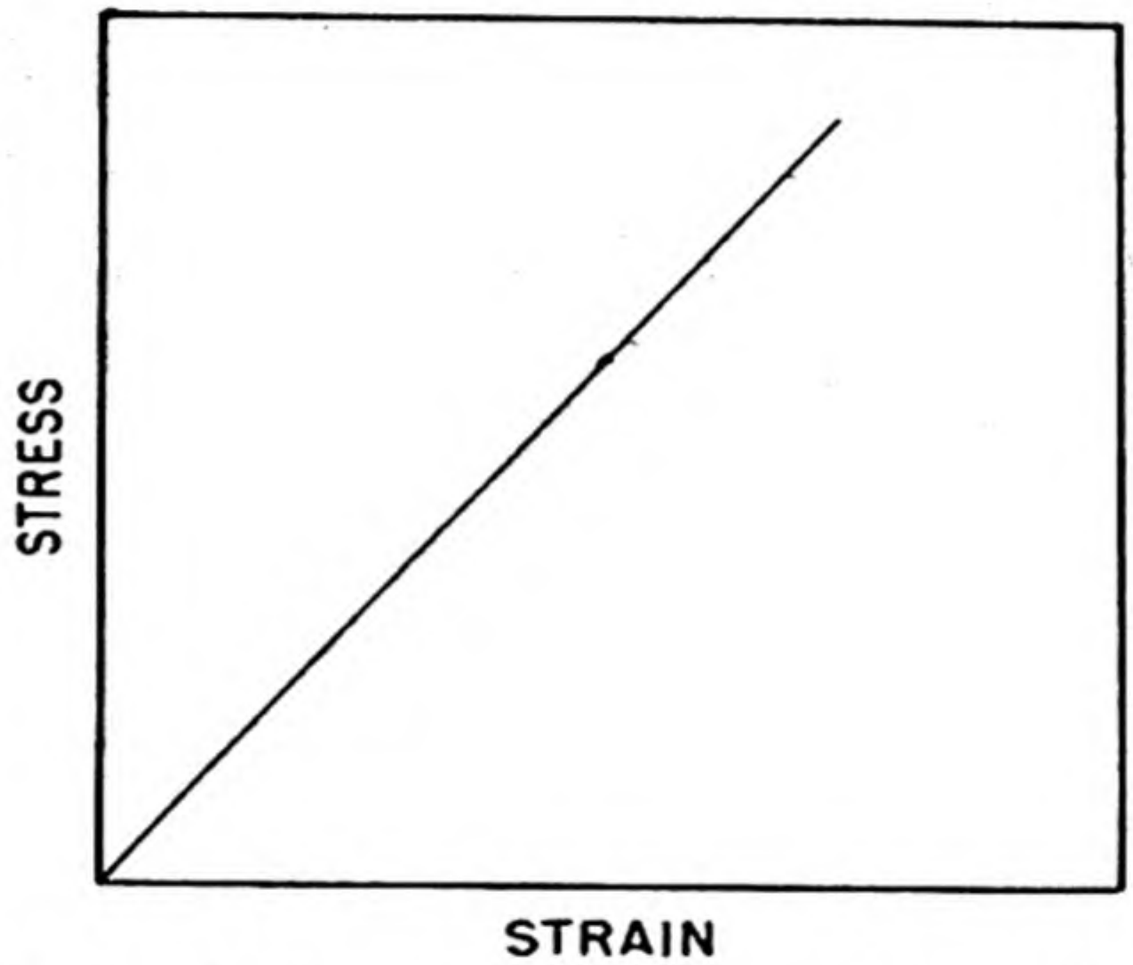


Figure VI-10. Stress-strain diagram for a Hooke body.

slope is represented by a Young's modulus S. Let the original film thickness be indicated by h_0, and let the film thickness be h upon subjugation to a stress F. The elongation λ, a dimensionless quantity, is defined by

$$\lambda = (h - h_0)/h_0 \tag{32}$$

The maximum film thickness h_m, corresponding to a maximum elongation λ_m is obtained at the maximum stress F_m just prior to rupture. The energy of elongation E_v may then be calculated according to the relation:

$$E_v = \int_0^{h_m} F dh = \int_0^{h_m} S\lambda dh = \int_0^{\lambda_m} S\lambda h_0 d\lambda = {}^1/_2\, h_0 S\lambda_m^2$$

Thus:

$$E_v/h_0 = {}^1/_2\, S\lambda_m^2 \tag{33}$$

Identifying for this approximation the transferred film thickness with the actual film thickness, a procedure allowed where only the order of magnitude is of interest, we find

$$E_v/h_0 \underline{\underline{\infty}}\ D_v = {}^1/_2\, S\lambda_m^2 \tag{34}$$

Since the film is incompressible, the shear modulus is equal to one-

third of Young's modulus of elasticity. Thus

$$G = {}^2/_3 D_v/\lambda_m{}^2 \tag{35}$$

For a numerical evaluation of G it is thus necessary to know the maximum elongation λ_m just prior to film separation. Tests with rotating rollers, such as reported by Sjodahl,[11] show that for conventional inks λ_m is generally between 3 and 10, although for inks with rubbery vehicles λ_m may be much larger. Since the tack energy density for most inks is between 10^7 and 10^9 ergs per cm.^{3}, the shear modulus G has a value estimated to be of the order of 10^6 to 10^8 dynes per cm.^{2}.

The maximum stress F_m necessary to cause film rupture may now be calculated.

$$F_m = S\lambda_m = 3G\lambda_m \tag{36}$$

and thus:

$$F_m = 2D_v/\lambda_m \tag{37}$$

For most commercial inks the maximum stress F_m appears to have an order of magnitude of 10^7 to 10^9 dynes per cm.^{2}. This value indicates that the maximum shearing stress to which an ink is subjected in a press may be exceedingly high. It occurs, however, only for an extremely short period of time, just prior to filament rupture.

The method of calculating the shear modulus from tack energy densities may be checked by the direct method developed by Mason.[12] This method uses shear vibrating crystals, which are immersed in the liquid. The resonant frequency of the immersed crystal is measured. The viscous as well as the elastic response of the liquid may then be calculated from the data obtained.

Two printing ink vehicles were investigated at a frequency of 19.7 kilocycles per second, corresponding to a stress duration of 5.5×10^{-5} second.[13] Such a stress duration is of the same order of magnitude as the stress duration in high-speed printing, where half-tone dots are separated in periods of time of 10^{-4} to 10^{-5} second. The results obtained by Mason are indicated in Table VI–2, together with the moduli calculated from tack energy densities by means of equation (35).

[11] L. H. Sjodahl, *Am. Ink Maker, 29* (3), 31 (1951).
[12] W. P. Mason, *J. Colloid Sci., 3,* 147 (1948).
[13] W. P. Mason, private communication.

In view of the character of the approximation, meant only to indicate the order of magnitude of the modulus, the results are satisfactory. It thus appears that the viscoelastic theory of film separation permits the correct prediction of the shear modulus G.

TABLE VI–2

Observed and Calculated Data for the Modulus G

	Mineral oil	Bodied linseed oil
Viscosity (poises at 25° C.)	63	65
Tack energy density, ergs/cm.$^3 \times 10^{-7}$	1.67	1.75
Calculated modulus G, dynes/cm.$^2 \times 10^{-6}$	4 – 16	5 – 18
Observed modulus G, dynes/cm.$^2 \times 10^{-6}$	7.85	15.8

From the established value for the modulus the relaxation time may now be calculated for printing inks according to equation (31). For an average ink, with a viscosity of between 10 and 500 poises, the relaxation time appears to be of the order of 10^{-4} second. The stress duration in high-speed printing may be an average of the order of 10^{-4} to 10^{-5} second. We must conclude that in printing the reaction to stress is both of a viscous and an elastic character, but the elastic component is dominant. At low speeds viscous inks with a high modulus are used, whereas at high speeds more fluid inks with a lower modulus are employed. This effect reduces the change in relaxation time with change in speed in commercially used inks. With the same ink, however, the higher the speed, the more pronounced is the elastic response to stress.

6. Molecular Concept of the Mechanism of Film Separation

In the process of film separation the ink film is elongated and finally ruptures. In rapid separation the elongation of the filaments is a result of a viscoelastic response of the liquid to stress. The rupture energy, always less than the surface energy, is a negligible part of the total energy used for film separation. The bulk of the energy is required in the process of film elongation.

Instantaneous elasticity in brittle solids gives rise to a modulus of elasticity of the order of 10^{12} dynes per cm.^{2}, only slightly affected by temperature changes. This type of elasticity results from stress deformation of primary bonds and angles as well as from displacement of particles against the van der Waals forces,

Elastic responses to stress of a different nature may occur in materials consisting essentially of large, highly elongated molecules. Such a behavior is especially pronounced in rubbery materials and usually is connected with a modulus of elasticity of the order of 10^6 dynes per cm.^{2} which increases proportionally to the absolute temperature. This mechanism, known as configurational elasticity, is a process connected with the orientation, alignment, and elongation by uncurling of long chain molecules. Configurational elasticity gives rise to a retarded elastic effect, since the stress relaxation occurs by a time-consuming diffusion process of the individual segments of the chain molecules into unstrained positions.

In liquids consisting of medium and longer chain molecules subjected to shearing stresses of brief impulsive or rapidly oscillating character, another type of shear elasticity exists, identified by Mason[14] as a Maxwell type of viscoelastic behavior. This elasticity is characterized by a modulus of the order of 5×10^6 to 5×10^8 dynes per cm.^{2} at ordinary room temperatures for frequencies of the order of 10 to 100 kilocycles per second, corresponding to an impulsive stress of a duration of 10^{-4} to 10^{-5} second. The logarithm of this modulus is inversely proportional to the absolute temperature. Measurements in polystyrenes and polyisobutylenes have shown that this rigidity occurs both in polymer solutions and in liquid polymers, although the modulus in solutions decreases markedly with decreasing polymer concentration.[15]

The mechanism of this response to stress appears to be connected with a composite motion of the molecular chains, which includes hindered rotations within chains as well as interaction of small segments between chains. This type of elasticity is not an equilibrium condition, since for the short impulses considered equilibrium is not established and the reaction depends on the nearest neighbors. If sufficient time is given, however, the normal configurational type of elasticity will prevail.[16]

At frequencies higher than 100 kilocycles per second, corresponding to stress impulses of a duration below 10^{-5} second, the indi-

[14] W. P. Mason, *J. Colloid Sci., 3,* 147 (1948).
[15] J. D. Ferry, *Ann. N. Y. Acad. Sci., 44,* 313 (1943).
[16] W. P. Mason, *J. Applied Phys., 73,* 1074 (1948).

cated motions cannot take place and the rigidity approaches the value for an elastic solid.[17]

The modulus connected with the nonequilibrium shear stiffness shows a remarkable analogy with viscosity in that its magnitude as well as its temperature dependency are closely related to those of viscosity. The stress relaxation of this mechanism, according to Ferry,[18] involves most likely a similar kind of molecular motion as viscosity.

From the foregoing it must be concluded that the viscoelastic responses to stress found to exist in printing ink films can be neither of the simple elastic solid nor of the configurational elastic type. For the elastic solid type the modulus would be much higher than actually found and hardly affected by temperature. For configurational elasticity the modulus would increase with increased temperatures instead of showing a pronounced decrease.

It is not difficult to identify the elastic response to stress of the ink film with the nonequilibrium elasticity, characterized by chain rotation and interaction of neighboring chain segments, as previously discussed. The duration of the stress impulse, of the order of 10^{-4} to 10^{-5} second, is of the correct order of magnitude for this type of stress relation, and the modulus is of the same order of magnitude as found by Mason[19] in direct measurements by means of transverse vibrations induced by piezoelectric crystals in long chain molecules.

The proposed mechanism for the film separation is the key to the influence of the film thickness. The energy required for the composite chain motion must be proportional to the number of molecules subjected to stress and thus to the volume energetically involved. Per unit area this energy will therefore be directly proportional to that part of the film which reacts to stress. The question whether the entire film or only part of the film is energetically involved in the film separation needs further elucidation.

In a solid film showing instantaneous elasticity the entire material is obviously strained by a stress. This type of elasticity, however, is not of any significance in the ink film. Partial involvement of the film, on the other hand, may be expected in the stress relaxation process previously indicated for film separation.

[17] W. P. Mason, *J. Applied Phys., 75,* 936 (1949).
[18] J. D. Ferry, *Ann. N. Y. Acad. Sci., 44,* 313 (1943).
[19] W. P. Mason, *J. Colloid Sci., 3,* 147 (1948).

In the rolling cylinder apparatus the stress exerted on the film must be considered an impact load, which necessarily creates a vibration. This vibration starts as an impulse and may be propagated as a shear wave of a frequency at least of the order of 10^4 cycles per second, in view of the stress duration period.

It is known that such shear waves are rapidly damped. Their critical damping distance is of the order of one wavelength. Experiments indicate that a complete saturation of the damping of such waves may even occur within a few microns.[19]

In our tests the pressure and therefore the amplitude of the vibration are rather low. Under these conditions the saturation of the damping of the oscillation in the filaments takes place at a short distance from the impacting roller, at a fraction of the total film thickness. Rupture will occur at the maximum elongation, causing separation and transfer of the vibrating parts of the filaments. At higher printing pressures and resulting increased amplitude, effective damping is materially reduced, in turn leading to an increased film transfer.

The mechanical work taken up by the ink resides in the transferred layer. The tack energy density is therefore proportional to the transferred film thickness. This proportionality is thus a direct consequence of the process of film separation.

The influence of the rate of film separation upon tack energy is the result of the change of ink transfer at different speeds. The fraction of the ink film transferred to the paper appears to be approximately inversely proportional to the speed. This, in turn, leads to a direct proportionality between tack energy density and rate of film separation. At higher pressures, however, a saturation of the effect occurs, and the proportionality between transferred film thickness and reciprocal rate of film separation no longer remains valid. Ultimately the film is then split evenly between identical surfaces, with some modification for surfaces differing in absorbability and roughness, as will be more fully discussed in Part II.

7. Tack and Viscosity

From experiments it appears that tack energy density depends on the plastic viscosity and not on the apparent viscosity of the ink. In attempting to explain this fact, two different effects of high speeds in printing must be distinguished. In the first place, at high speeds the ink is subjected to high shearing stresses, causing the more or less

complete breakdown of the loosely connected particle arrangement known as structure. In the second place, at high speeds the rate of film separation is high, resulting in a more pronounced elastic response of the ink film to stress. Press speed, therefore, determines the character of the film separation. Both phenomena, structure breakdown and film separation, are not necessarily tied together, since it is possible, in principle, to print at any desired rate of film separation with an ink in any structural state of breakdown by operating the ink distribution mechanism of a press independently of the inking mechanism.

It is recognized that commercial inks do not show a very rapid rebuilding of a broken-down structure, and inks subjected to high shearing stresses will generally remain in a structure-free state for a period of time of minutes, long enough to operate the rolling cylinder tackmeter.

There is, in addition, another important consideration. One of the results of the structural buildup in inks is that an applied stress is partly used to break up the existing structures. The plastic viscosity is the resistance to viscous deformation at high shearing stress, in the absence of structures, while the apparent viscosity at lower shearing stresses is the result of a mixed response to stress, partly the breaking up of structures, partly viscous flow. It now becomes apparent that the ink cannot respond to a brief impulsive stress of the order of 10^{-4} second by the destruction of the structures. The time scale of the action is too rapid for a viscous as well as for an equilibrium configurational elastic response and evokes only local chain motions. Such rapid impulses do not, therefore, cause a breaking of the structures in non-Newtonian dispersions, the relaxation times of which are usually much greater than 10^{-4} second.

While basically the mechanism of stress response in the ink film has been ascribed to the reaction of longer chain organic compounds, the presence of pigments and other ink constituents will affect the magnitude of the stress response. The stress relaxation mechanism involves the same type of molecular motion as the viscous deformation. It is therefore understandable that the presence of pigments and other ink constituents influence the activation energy of the composite chain motion responsible for the stress relaxation by modification of attractive forces, by steric hindrance, or by other mechanisms, in the same manner as the activation energy of the

viscosity is modified. Consequently, although the response to stress is basically a reaction to stress of the longer chain vehicle constituents, the influence of other materials present may be very pronounced. A similar effect is observed in rubber, where the mechanism of response to stress is basically a reaction of the long chain hydrocarbon molecules, but may be modified markedly by other constituents, such as carbon black and other pigments.

It is possible to prepare viscous liquids which cannot react elastically to stresses of a duration of 10^{-4} to 10^{-5} second. Such systems may be made by incorporating pigments, such as clay and carbon black, in liquids such as water, ethanol, or similar materials consisting of small molecules. The resultant dispersions show a pronounced resistance to flow; yet they are devoid of all tack. This is in agreement with the results of the present investigation, indicating that not the viscous flow, but a viscoelastic process is responsible for tackiness. The observation that all adhesives are of a high molecular nature emphasizes this conclusion.

It was found that while the tack energy density increases with the viscosity of the liquid, all liquids investigated were of a high molecular nature and consisted of molecules with long carbon chains. In all these cases the stress relaxation both by viscous flow and by the described viscoelastic reaction depends on the same molecular motion. The coefficient of viscosity in all experiments described therefore affords simply a convenient measure for the resistance to stress relaxation by the viscoelastic process. This explains the paradox that while the stress relaxation occurs by a viscoelastic effect, the coefficient of viscosity seems to be a determining factor in the tack energy.

An interesting observation is that tackiness seems to be accompanied by "stringiness," the property of a liquid permitting it to be drawn out in strings. Viscous aqueous pigment dispersions are not only nontacky, but they also cannot be drawn into strings. It does not seem improbable that both tackiness and stringiness of liquids are the result of similar viscoelastic reactions of longer chain molecules.

D. INK FLYING

1. Phenomenon of Flying

Ink flying, also known as misting, spraying, clouding, or fogging, is caused by ink in the form of small droplets being ejected from

a moving press. The mist is not only extremely annoying to personnel, but it also contaminates the entire pressroom and in some instances becomes a serious fire hazard. Ink flying may be one of the major factors limiting the speed of newspaper printing.

The literature on ink flying is a maze of vague, ambiguous, and even contradictory information which generally is confusing because of the lack of scientific experimentation. Most of the information consists of general observations of the behavior of various inks in pressrooms in which conditions determining the intensity of ink flying are not controlled and quantitative conclusions are impossible. If studies of the prevention of ink flying are to be successful, they must investigate the cause as well as the various influencing factors.

2. Cause of Ink Flying

It has been observed that ink is never flung from a rotating roller by a centrifugal force. A simple experiment, advantageously carried out with an inkometer or with any other set of rollers rotating at variable speed, has shown that without roller contact a film of ink, of a thickness comparable to the film thickness used on the press, is not thrown off the single roller, even at peripheral speeds far exceeding those on high-speed presses. As soon as a second roller was brought into contact with the first, ink flying was observed at high speeds. Ink flying is therefore connected with ink transfer, and it is justifiable to state that in the absence of ink transfer no flying occurs.

As discussed previously, the phenomenon of rapid film separation is not caused by liquid flow but by a rupture, in a solid pattern, against elastic forces. Ink on a rapidly rotating pair of contacting rollers is drawn out in filaments and ruptured.

Upon rupture, the ink filament will not, as a rule, break into two equal parts, but the location of the break is usually eccentric. This conclusion may be derived from the fact that the fraction of ink transferred usually differs considerably from half the total quantity. It is determined by such factors as pressure, speed, nature of surfaces, and characteristics of the ink, as will be discussed later.

If a break in the filament occurs at two places simultaneously, the middle part will be released upon retraction of the other parts of the filament. This quantity of ink will take the spherical shape, as a result of the surface tension, and if not caught by the inked rollers, will continue its existence as a free droplet, ejected by the press.

It thus appears that ink flying is caused by the ejection of ink droplets by the press, formed by simultaneous multiple rupture of ink filaments.[20] Quantitatively it appears that the number of such multiple ruptures necessary to explain the phenomenon of ink flying is very small, since the quantity of ink generally ejected from the press is only a very minute fraction of the total quantity of ink transferred. The fact that filament retraction occurs in such a short period of time makes the statistical chance of multiple breaks occurring rather small.

3. Electric Charge

It was discovered in 1935 that the ink particles ejected from the press carry an electric charge.[21] Later it was found that both positively and negatively charged particles may exist in an ink mist.[22]

It has been shown that when water is dispersed in fine particles in a gas phase, the resulting drops are positively charged, while the corresponding negative charge is taken up by the atmosphere.[23]

The separation of the charges must be attributed to the shattering of the exterior liquid film carrying the electric double layer present in the boundary of filaments and drops. The destruction of this thin liquid film causes the separation of the electric charges, part of which remain in the ink, while the corresponding charge of opposite sign is dissipated in the air, a phenomenon known as ballo-electricity.

The retracting parts of the ruptured filaments will carry their electric charge to the rollers or to the moving paper web, causing the accumulation of electric charges on roller and paper. An electrically charged ink drop, upon being released from a filament showing multiple rupture, faces rollers of a charge of equal sign. The particle will therefore be repulsed and ejected into the open space, thus greatly reducing its chance of being taken up by the rollers.

Microscopic examination of ejected ink droplets often reveals a characteristic migration of carbon black particles toward the center and toward the periphery of the drop. The carbon black particles of an ink always carry an electric charge, positive or negative, but which is neutralized by the counter ions in the electric double layer. If the drop itself carries an excess of charge on its surface, cataphore-

[20] A. Voet, *Patra J., 13* (1), 17 (1950).
[21] W. T. Diefenbach, *Am. Ink Maker, 13* (9), 21 (1935).
[22] C. C. Mill, *Patra J., 4* (5), 76 (1941).
[23] C. Christiansen, *Ann. Physik,* (4) *40,* 122 (1913).

sis, the migration of suspended particles of the carbon black under the influence of the electric charge, will occur. The observed migration of the positively and negatively charged particles is in opposite directions, toward and away from the periphery. Thus, the carbon black migration is a direct proof of the presence of electric space charges in the drop.

The ejected charged particles show little tendency to particle union, owing to the mutually repulsive electric forces. The smaller charged particles will thus have a tendency to drift, in an expanding cloud, in the pressroom.

A distinction between "misting" and "flying" has often been made, but it has no fundamental significance, since both phenomena result from the same filament disintegration. The term misting is more appropriate for smaller particles with a high electric charge, which do not settle easily. Flying applies to the spreading of larger particles, or particles which carry only small electric charges and which collect, usually, near the press. No precise information is available about the factors determining the size and charge distribution of the particles resulting from the disintegration of ink filaments.

4. Factors Influencing Ink Flying

The many varied and sometimes contradictory pronouncements regarding the influence of external and internal factors upon ink flying are better understood by taking into account the complex origin of ink flying. Let us first examine the external factors, of which the electric charge is the most important.

The magnitude of the charge of the particles of a given ink depends primarily on the rate of film separation and therefore directly on the press speed. In addition, temperature and humidity of the air are of great importance.

It may be said that the press speed is the most important factor in ink flying. At lower press speed, flying is usually negligible. At intermediate speeds, above 1000 ft. per minute, flying is a serious problem in newspaper printing. Experiments have shown that at speeds exceeding 1500 ft. per minute newspaper printing is hardly possible, owing to ink flying, which then becomes one of the major problems. It must be stated, however, that the change in ink characteristics necessary to print satisfactorily at high speeds is favorable to the promotion of flying.

Low absolute humidity is a favorable condition for the generation of electric charges. Thus, cold dry weather promotes ink flying, although the influence of the increased ink viscosity counteracts the increased charges to some extent. The presence of moisture, however, tends to reduce electric charges and acts to diminish flying.

Imperfect mechanical conditions, such as a faulty roller setting, worn rollers, and worn and uneven running presses, will generally increase ink flying. This effect must be ascribed to the increased thickness of the ink film usually carried in older and defective equipment, since it is evident that flying is greatly increased with thicker ink films, which show a much more pronounced ink filamentation.

An important factor in the evaluation of ink flying is the presence of air currents. Usually excessive flying in a particular location is due to local air currents, which carry the particles toward the observation post. Relief from this condition often occurs as a result of a change in the air currents, although actually no decrease in flying takes place. The quantitative evaluation of ink flying by comparing the number of drops fallen in a given location in a certain period of time per unit surface area may be completely misleading, unless the experiment has taken place under specified conditions, usually not possible in a pressroom. Tests in commercial pressrooms have significance only when a large number of tests are taken over longer periods of time and the results are properly interpreted.

Of a number of properties playing an important part in determining internal ink characteristics the rheological ink properties are examined first.

Elastic forces in the liquid are the more pronounced the more viscous the ink. In viscous ink, all other characteristics being equal, stronger elastic forces tend to shorten the lifetime of the filaments, resulting in reduced flying. On the other hand, the longer the filament is drawn out before film separation, the greater is the chance of multiple rupture and the greater the tendency to flying to be expected. This has been confirmed experimentally.[24]

Generally, the higher the temperature in laboratory tests, the more pronounced is the ink flying. This is in accord with the observation that ink flying is greatly increased during the hot season.

[24] L. H. Sjodahl, *Am. Ink Maker, 29* (3), 31 (1951).

The existence and magnitude of a yield value seem hardly of importance for ink flying. This is in agreement with expectation, since flying occurs in inks subjected to shearing stresses, where no structural buildup responsible for the occurrence of a yield value actually exists.

The surface tension of an ink is not expected to influence ink flying. This is obvious from the consideration that the elastic tensions involved in the filament elongation are of a much higher order of magnitude than the surface tension. The action of the surface tension to reduce the surface area of the filament is thus completely negligible compared with the action of the elastic forces. This was shown experimentally by reducing the surface tension of a news ink appreciably by the incorporation of traces of silicones, without influencing flying tendencies in the least.

An important factor is the electric conductivity of the ink. This may be concluded from the fact that a conductive ink cannot become electrically charged on a grounded press. Water-based inks, therefore, which are usually conductive, do not show any flying even at high speeds.

The conductivity of conventional oil-based inks is low. The most conductive are those comprising carbon black, the conductivity of which is of the order of 10^{-13} reciprocal ohm, classifying these inks between semiconductors and insulators. Upon increasing the carbon black contents of an ink, the conductivity increases. One would therefore expect a tendency to reduce flying by using inks with higher carbon content. Unfortunately, however, when the carbon content is increased, nearly every other factor influencing ink flying is changed, making a study of the effect of conductivity impossible.

The dielectric constant of the ink appears to be a factor which has a bearing upon ink flying. In a charged ink filament fraction about to be detached from the rest of the filament, repulsive forces exist which greatly facilitate separation of the filament, promoting multiple ruptures. In a material of a high dielectric constant such repulsive forces are greatly reduced, since in a dielectric the electric forces are inversely proportional to the magnitude of the dielectric constant. Consequently, the higher the dielectric constant, the less ink flying is to be expected.

5. Prevention of Ink Flying

(a) **Mechanical.** The shielding of press rollers by means of metal shields is an important contribution to efforts to minimize the effects of ink flying. By this simple protection device the larger ink droplets are collected. Such a shield, however, does not collect the smaller charged particles.

(b) **Physical.** A device to collect mist particles is described in U. S. Patent 2,096,164 of W. T. Diefenbach. It consists basically of a copper wire net placed around the locations where ink flying originates. The net is electrically charged with a charge whose sign is opposite to the sign of the charge of most of the ejected ink particles. The net therefore precipitates and collects the ink mist, at least those particles which have a charge opposite to the net charge. Theoretically the principle of the charged net appears to be sound, but its application has not seemed practicable, and electrostatic ink precipitators are not actually in use on a commercial scale.

Since the electric charge was found to be a major factor in causing ink flying, investigations have been directed toward minimizing the effect of the charge.

Attempts were made to prepare conductive inks, which would result in the complete loss of the electric charge in a grounded press. It has not been possible, however, to prepare inks with an oily vehicle which are conductive under stress. The incorporation of the so-called conductive blacks leads to the formation of inks which are conductive only while at rest. Most of the conductivity is lost when, under shearing stresses, the particle chains formed in the vehicle, which are responsible for the conductivity, are broken.

Variations in flow characteristics of conventional high-speed news inks, within the limits imposed by press requirements, do not lead to markedly reduced flying.

It was found, however, that emulsion inks of the water-in-oil type showed a reduced tendency to flying. The action of a quantity of water of as little as 5 per cent by volume is already noticeable. Larger quantities of water dispersed in the ink are increasingly effective.

Although the conductivity of water-in-oil emulsion inks does not differ appreciably from the conductivity of the oil inks, the dielectric constant of the emulsion inks is greatly increased. Water not only

has a dielectric constant nearly forty times as large as the dielectric constant of oil, but the particle structure formed in an emulsion ink with as little as 10 per cent water present also results in a dielectric constant which may be more than ten times as large as the value in the absence of water. The repulsive forces in the filaments are then markedly decreased, necessarily leading to a reduction in the number of multiple breaks.

In addition, there are indications that emulsion ink particles ejected from the press bear a considerably smaller average charge than ejected oil ink particles, owing to the changed phase boundary conditions, which apparently influence the ballo-electric charges. The repulsive forces between particle and rollers are therefore less pronounced and a greater fraction of the ejected particles is taken up by the rollers.

Emulsion ink particles ejected from the press do not show, upon microscopic examination, a migration of carbon black particles in the drop, indicating the absence of strong electric fields.

The incorporation of water into black news inks with the aid of conventional emulsifying agents leads to short buttery inks, which cannot be used in high-speed printing. Long chain nonaromatic amines of a particular chemical structure may be used to produce water-in-oil emulsion inks which have completely satisfactory rheological characteristics.[25]

To prevent fill-in of halftone plates, however, the particle size of the emulsified phase must be extremely small, since oversize particles cannot be tolerated. This poses a difficult problem for the commercial manufacture of emulsion inks, especially since the emulsion must remain unchanged after a prolonged storage, often at the high temperatures prevailing in press rooms. The inherent thermodynamic instability of emulsions will make it difficult to prevent gradual coalescence of the water droplets, resulting in the formation of highly undesirable larger water droplets under such conditions.

[25] A. Voet, U. S. Patent 2,450,534 (Oct. 5, 1948).

PART II

INK AND PAPER

CHAPTER VII

CHARACTERISTICS OF DISCONTINUOUS REPRODUCTION

A. INTRODUCTION

In the evaluation of type and line drawings the contrast with the background and the sharpness and the uniformity of the printed reproductions are indicative of their quality. With halftone reproductions rapidly becoming the most important element in publication printing, the accurate reproduction of halftones has become a major requirement in printing.

In evaluating a reproduction of a halftone the gradation of the tone value between highlights and shadows has real significance. An examination of the characteristics of halftone reproduction is therefore an essential part of the study of interaction of ink and paper.

Only the overall effect of the printed halftone reproduction appeals to the observer, but the general impression is conveyed by the blending of the individual effects of the units of the printed reproduction, the halftone dots. The characteristics of the dots, both in the ideal and in the practically obtainable form, lead to a better understanding of the essential factors determining the characteristics of the printed halftone reproduction in the various printing processes.

B. ORIGINAL AND REPRODUCTION

The ideal reproduction process produces an exact copy of any given original, which is always in a continuous tone. In view of the requirements of the inking mechanism of a press the image is necessarily broken up into the multitude of single and merged dots which form the halftone reproduction.*

Halftones are made from the continuous tone original by inserting a screen between the object and the photographic plate on which

*We shall refrain from a description of processes using a continuous plate, such as collotype, due to their relative unimportance in the field of reproduction.

the reproduction is to be made. It has been shown by Tritton and Wilson[1] that the optical characteristics of continuous tone originals are essentially different from the characteristics of discontinuous reproductions. A simple way to compare the optical properties of original and reproduction is to plot the optical densities of both against each other in a diagram. Optical densities can be measured easily on a photographic plate by determining the light transmission values. The optical density of a transparency is defined as the inverse value of the logarithm of the light transmission; the optical density of an opaque image is defined as the logarithm of the inverse value of its reflectance.

In Figure VII–1 the straight lines represent the ideal reproduction, obtained by plotting optical densities against the identical values of the continuous tone negative. It may be observed that the optical characteristics of an ideally perfect discontinuous halftone negative, represented by the deepest curve, are quite different from the properties of the continuous tone negative. The curve representing an average actual screen negative, shows that its optical properties are much more like those of the continuous original than the ideal negative. From this it appears that a better reproduction can be had with an actually made halftone plate than with the ideal perfect plate.

The differences in optical density between a continuous original and an ideal discontinuous reproduction are caused by the method itself, which necessitates the placing of a screen in front of the camera, resulting in negative dots of too large area throughout most of the range. Consequently in the positive the dots are too small, even in the ideal case.

In the practical preparation of typographical plates, carried out by an etching process, it appears that etching liquids inevitably have a tendency to attack the sides of the dots. This phenomenon, known as undercutting, may be reduced, but by no means eliminated, by the application of inert powders during the etching process. As a result, the etching process leads to an additional decrease of the dot sizes, and it would seem that actual halftones would compare even less favorably with the original than ideal halftone plates. Fortunately, however, the size of the printed dot reproduction is considerably larger than the size of the actual halftone dot, due to a phenomenon known

[1] F. J. Tritton and E. T. Wilson, *Phot. J., 79,* 396 (1939).

as ink displacement or "squash." Ink squash is a result of the printing pressure which causes some of the liquid ink to be squeezed from the center of the surface of the dot to the periphery. If this displacement is limited and leads to sharply confined dots, or sharply confined interstices for merged dots, the reproductions show increased printing areas and are characterized by optical density curves, such as the one formed in Figure VII–1 by the curve of the actual screen negative,

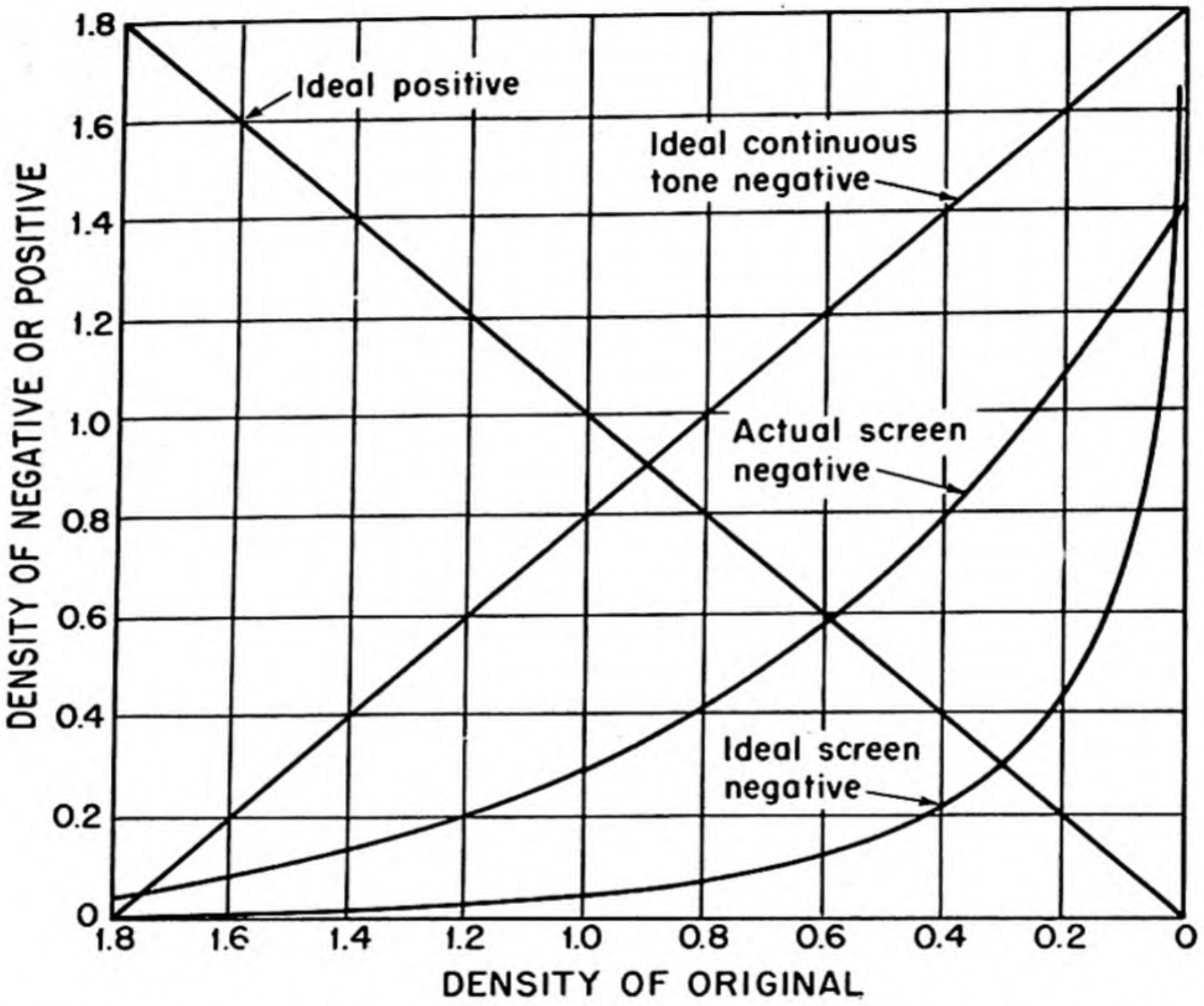


Figure VII-1. Optical densities of original and reproduction.[1]

much nearer in tonal gradation to the original than the ideal discontinuous tone reproduction made according to the conventional methods of producing screen negatives.

The effect of penetration of light into the paper is a complicating factor, since light does not emerge from the paper at exactly the same spot where it entered, so that some of the light which enters through a dot emerges through white paper. This increases the density of the middletones appreciably, especially for prints on uncoated papers. The effect is still further increased by multiple internal reflections.[2]

[2] J. A. C. Yule and W. N. Nielson, *Mod. Lithography, 29* (6), 55 (1951).

C. THE DOT SIZE

The greater the number of dots per square inch, the closer the optical characteristics of the ideal and actual reproduction approach the continuous original. It is therefore desirable, for a good reproduction, to have a fine halftone screen. In actual printing the dot size is limited by practical considerations, primarily by the paper and the printing process. For typographic newspaper printing 50–70 lines per inch will yield a fairly clear reproduction. A greater number of lines per inch is not satisfactory, because the lack of smoothness in the type of paper stock used in newspaper printing increases the degree of distortion of the dot reproductions.

Satisfactory commercial printing on better grades of paper are usually carried out with a screen of 120–150 lines. It is possible to use a much finer screen, up to 400 lines to the inch, but on account of the excessive care required in their preparation and handling, such fine screens are seldom used.

In the offset lithographic process dot distortions are minimized by the use of a resilient rubber blanket, and a screen finer than is generally used in typography results in a better reproduction on rough paper stocks. In the gravure process dot distortions do not seem to play such an important part, and excellent results are often obtained on the cheaper and rougher grades of paper with a relatively fine screen.

CHAPTER VIII

MICROSCOPY OF HALFTONE PRINTING

A. CHARACTERISTICS OF HALFTONE DOTS

The essential properties of halftone dots are advantageously examined with the aid of a light microscope. Bernstein,[1] in an extensive study of dot formation, recognizes two major factors, namely, sharpness of contours and uniformity of ink coverage. The sharpness of the dot contour is defined as the acuity of focus of the outline of the dot, while the uniformity of ink coverage is the evenness of ink distribution over the area occupied by the dot. Ideal sharpness of contours and uniformity of ink coverage will lead to sharpness in detail and fullness of contrast, both in individual dots in the 10–50 per cent coverage range as well as in merged dots in the 60–90 per cent coverage range.

Figure VIII–1A shows a section of a 133-line halftone screen, printed by a typographic flatbed press in black on coated stock, at a 25 × magnification. The sharpness of contour is excellent, but the uniformity of ink coverage is poor, as is shown more clearly in Figure VIII–1B where the magnification is 75 ×. In Figure VIII–1C a single dot is shown at a 700 × magnification. Similar results were obtained with all types of typographic inks, formulated on the basis of drying oils as well as heatset or moisture-set inks, on flatbed and on rotary presses. No differences in the dot characteristics appear between black inks and colored inks, and the individual dots showed the same basic properties as the merged dots.

A slightly different picture is shown by coldset inks, which are rather low in viscosity at printing temperatures. The dots are somewhat less uniform in coverage, but the sharpness of the dot contour has considerably increased owing to a pronounced but very uniform ink squash.

[1] I. M. Bernstein, *Modern Lithography, 25* (10), 46, 137 (1947); *Am. Ink Maker, 25* (10), 48 (1947).

As may be expected, the halftone dot merely accentuates a phenomenon observed with type and line cuts. For instance, Figure VIII–2 represents type taken from a conventional newspaper. The lack of both uniform ink coverage and sharpness of contour is plainly visible. On the other hand, Figure VIII–3 represents type taken from a newspaper printed with coldset ink. Here the ink coverage

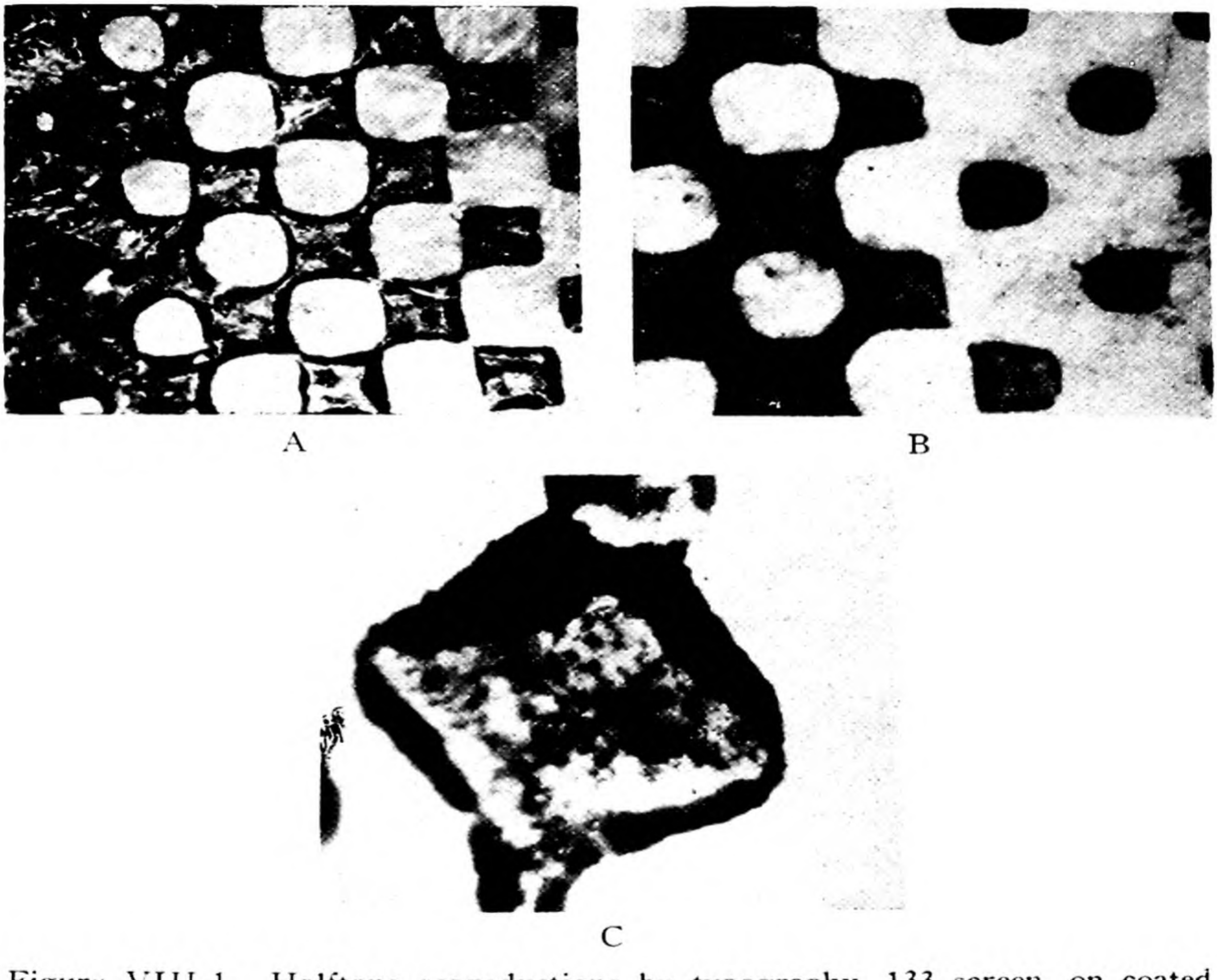


Figure VIII-1. Halftone reproductions by typography, 133 screen, on coated stock: (A) 25×; (B) 75×; (C) 700×.[1]

of the letter is even less uniform, but the sharpness of the contours is notably increased. The improved sharpness of coldset inks leads, as may be expected, to a marked increase in contrast and "sparkle" over conventional news ink, even on a rough stock. It makes it possible to use even a much finer screen for halftones, leading to a considerably improved reproduction with coldset inks.

In offset lithography the halftone dot is characterized by an outstandingly good uniformity of ink coverage, but by a poorly defined sharpness. This may be seen from Figure VIII–4A, which shows an example of a lithographic offset 133-line screen deep-etch halftone plate printed in black on a coated paper at a 25 × magnification. Figure VIII–4B shows the same screen at a 75 × magnification,

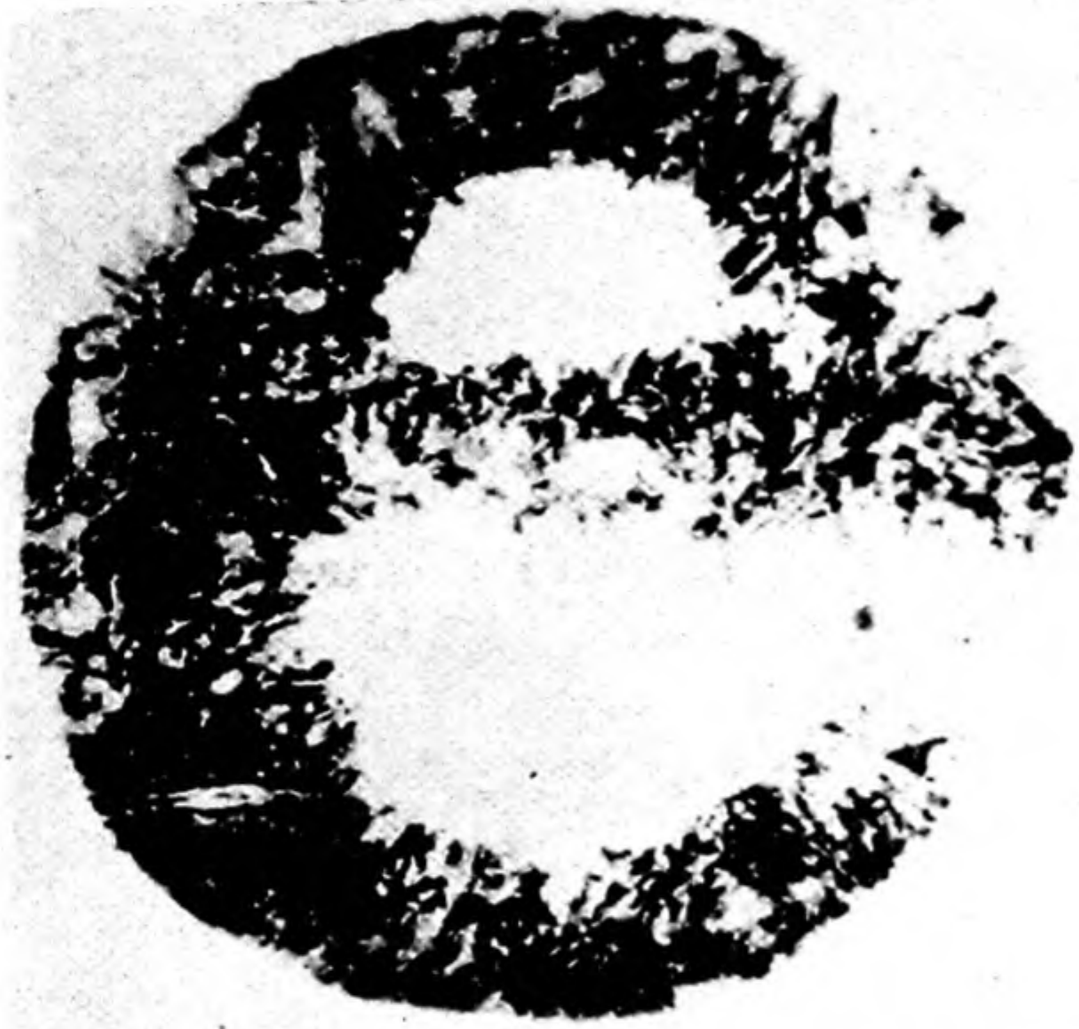


Figure VIII-2. Type reproduction from conventional newspaper. Magnification 35 ×.

Figure VIII-3. Type reproduction from newspaper printed with coldset ink. Magnification 35 ×.

and VIII–4C shows a single dot from the previous figure in a 700 × magnification. Again, these results are characteristic of all types of inks, of all colors, and of all types of lithographic printing presses.

The reasons for the dot properties are found in the nature of the reproduction process. In offset lithography the ink is transferred from plate to blanket and finally from blanket to paper. In this process the sharpness of contour is lost, but the uniformity of dot coverage is not affected on account of very uniform printing pressure resulting from the flatness of the plate and the resilience of the blanket. Consequently, in offset lithography, with its uniform dot coverage, a finer gradation of hue is possible in the reproduction than in typography. The tonal range, however, is considerably shorter than in typography. Typography is characterized by sharpness, contrast and sparkle, but a poor gradation of color hue; offset lithography yields softer prints, of a finer gradation of color hue, but lacking sparkle.

Offset type is equally characterized by a lack of sharpness, as may be seen from Figure VIII–7.

Figures VIII–5 and VIII–6 show enlarged four-color halftone reproductions in typography and in lithography respectively. The conclusions drawn from the single color photomicrographs appear to be fully applicable in multicolor prints.

In photogravure printing the size of the unit cell is generally a constant and only its depth varies. Figure VIII–8 shows a commercial black gravure print, demonstrating ill-defined contours and only a

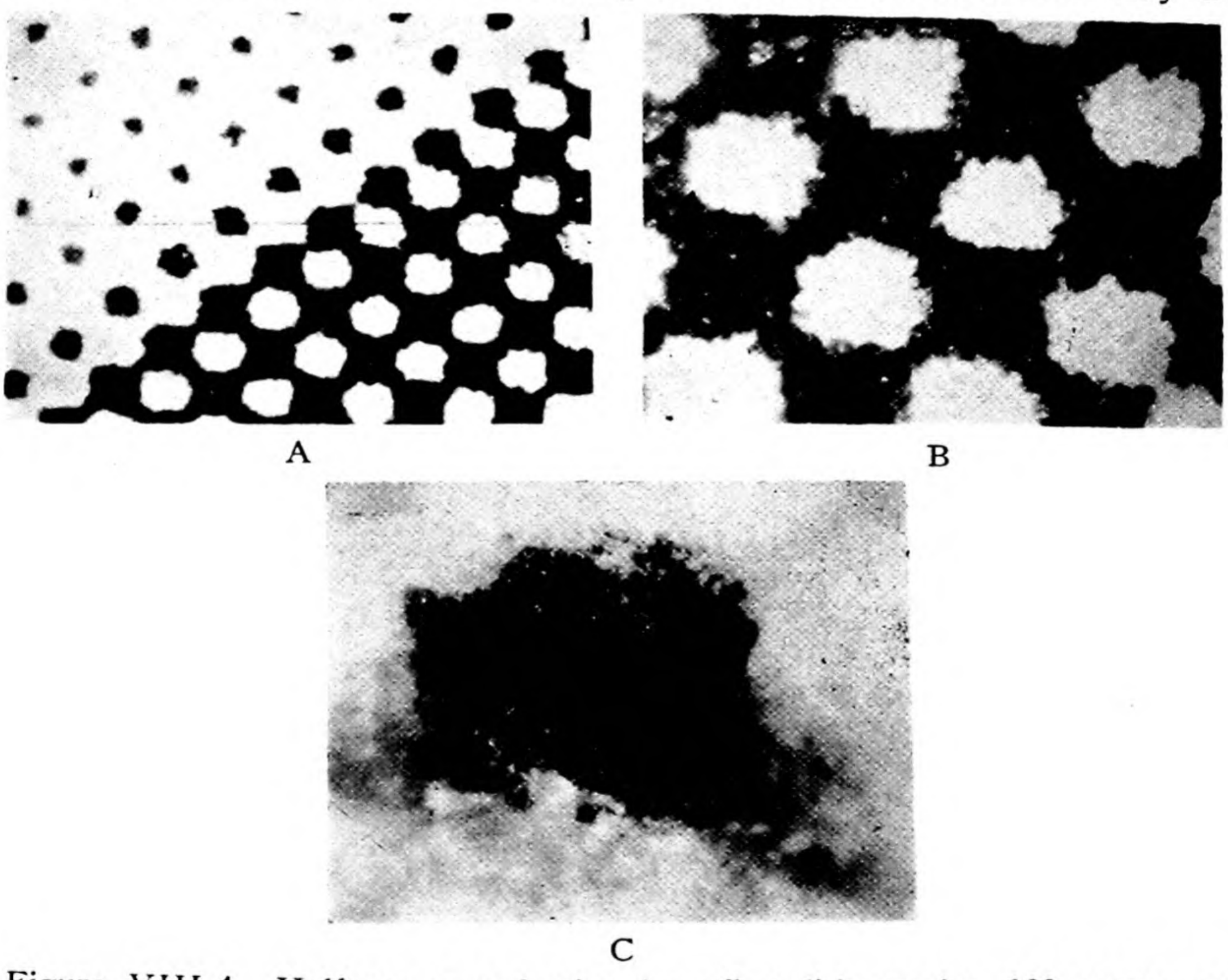


Figure VIII-4. Halftone reproduction by offset lithography, 133 screen, on coated litho stock: (A) 25×; (B) 75×; (C) 700×.[1]

fair uniformity. One would therefore expect a limited gradation of color hue and a lack of contrast. Actually, however, photogravure prints, particularly in color, show a marked contrast and sparkle. Bernstein[1] explains the apparent anomaly by the fact that in photogravure halftone printing the tonal range is quite short and the change

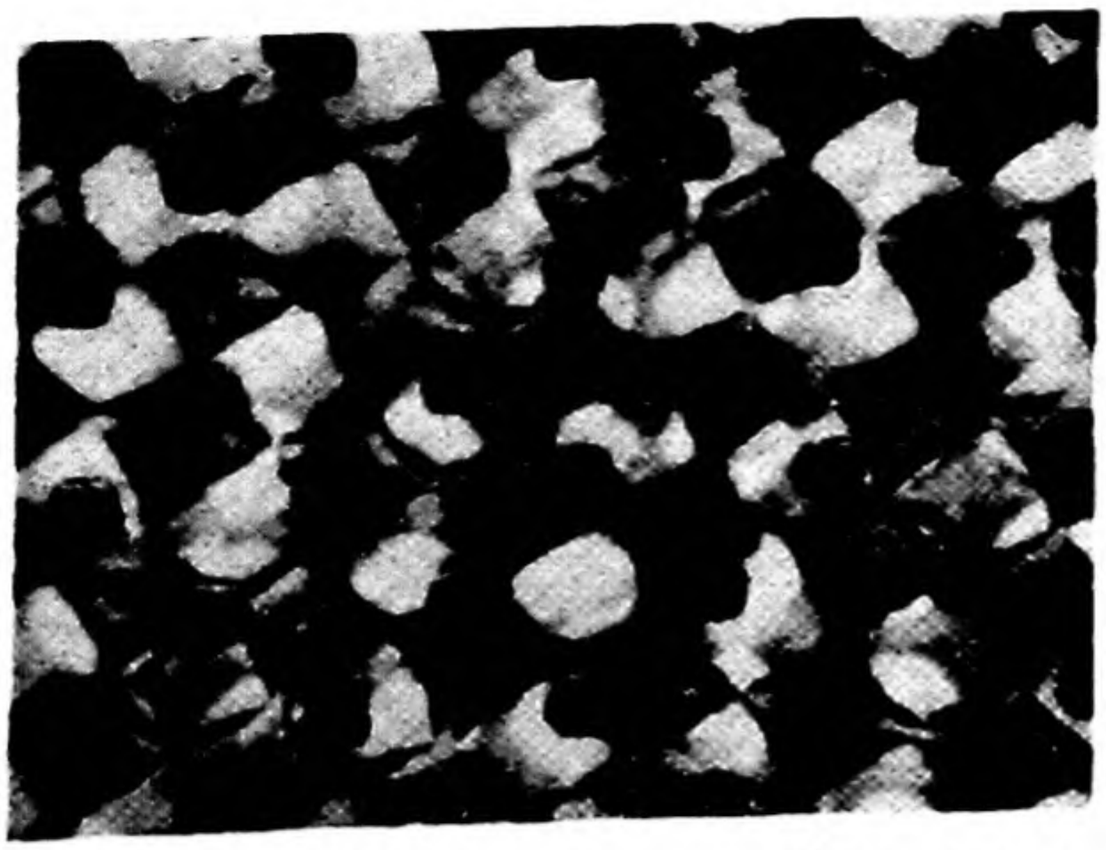


Figure VIII-5. Four-color typographic halftone reproduction.[1] Magnification 75×.

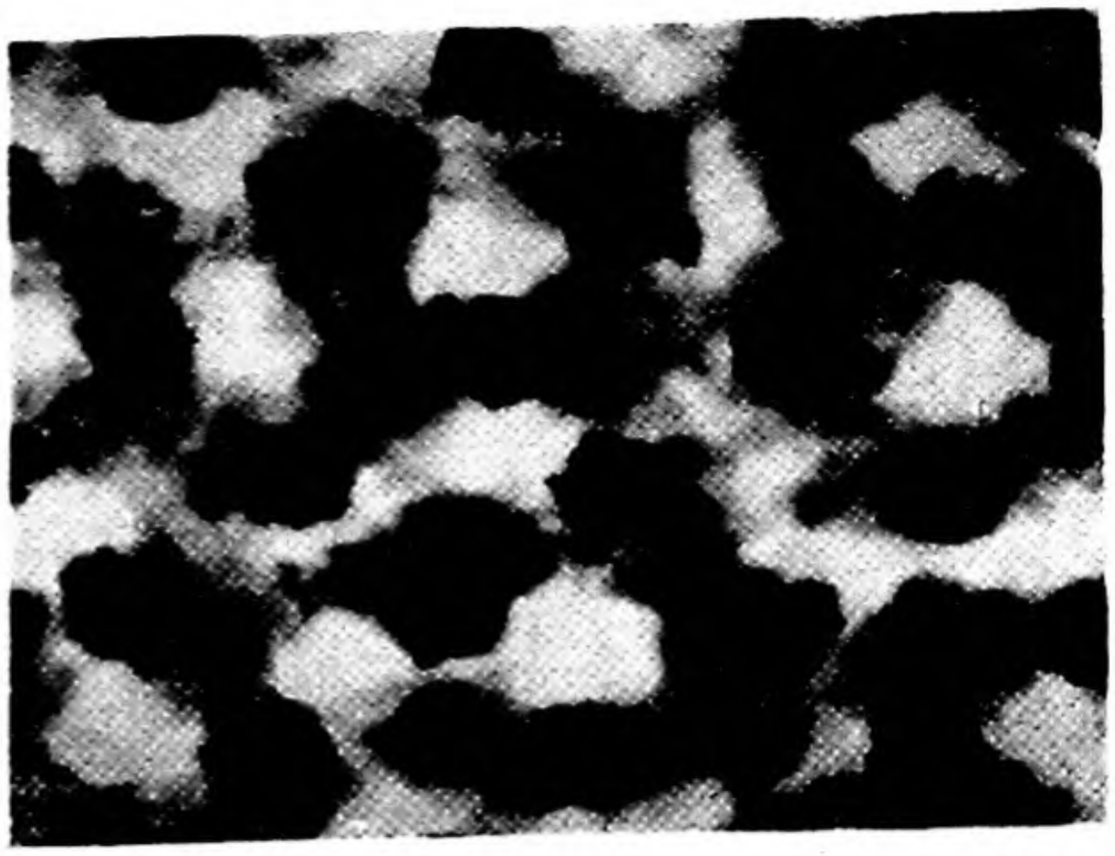


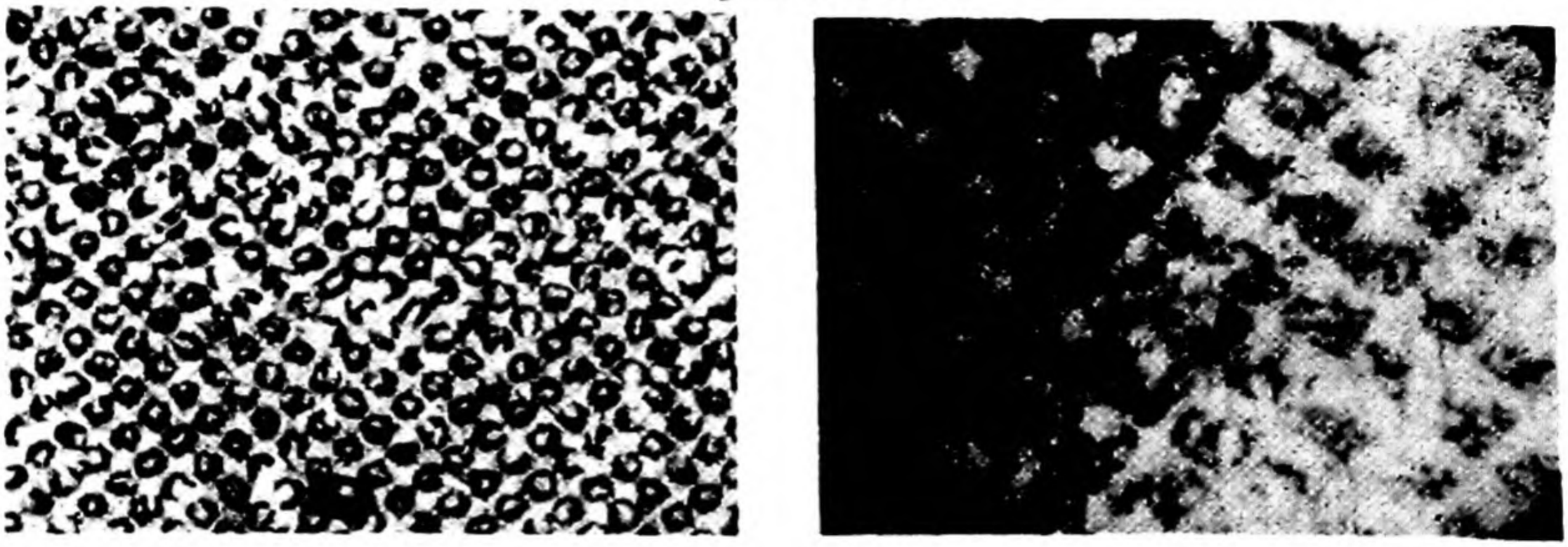
Figure VIII-6. Four-color offset lithography halftone reproduction.[1] Magnification 50×.

Figure VIII-7. Type reproduction in offset lithography. Magnification 30×.

from highlights to shadows takes only relatively few steps. As soon as the depth of the unit cell exceeds a certain limit, the amount of ink is too great, after transference to the paper, to indicate much, if any, gradation in tonal value. The result is therefore a depth of printing in the solids together with the natural gloss inherent in the inks, which yields the characteristic contrast of gravure printing. Owing

to the short tonal range, however, the quality of photogravure reproduction is inferior to that of either letterpress or offset.

In the Dultgen process of photogravure printing both the size and the depth of the cells may show a variation. This results in a longer tonal range as well as in an increased sharpness of dot contours, yielding a distinctly superior reproduction.



A B

Figure VIII-8. Halftone reproduction by rotogravure on roto stock: (A) 15×; (B) 37×.[1]

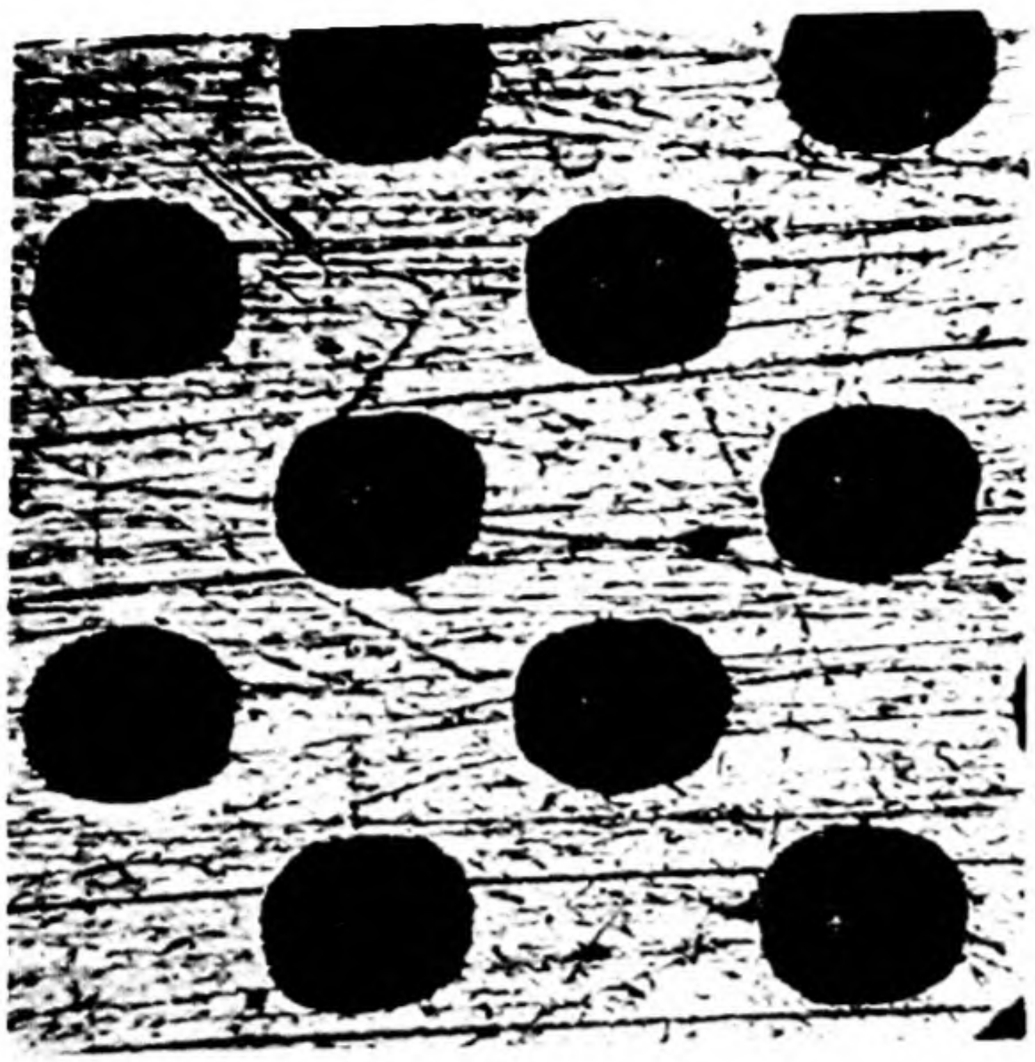
The examination of the photomicrographs of halftone dots shows beyond doubt different characteristics produced by the various printing processes which will allow the skilled observer to draw conclusions about the particular process used in a reproduction.

B. DOT DISTORTION DUE TO PAPER INFLUENCE

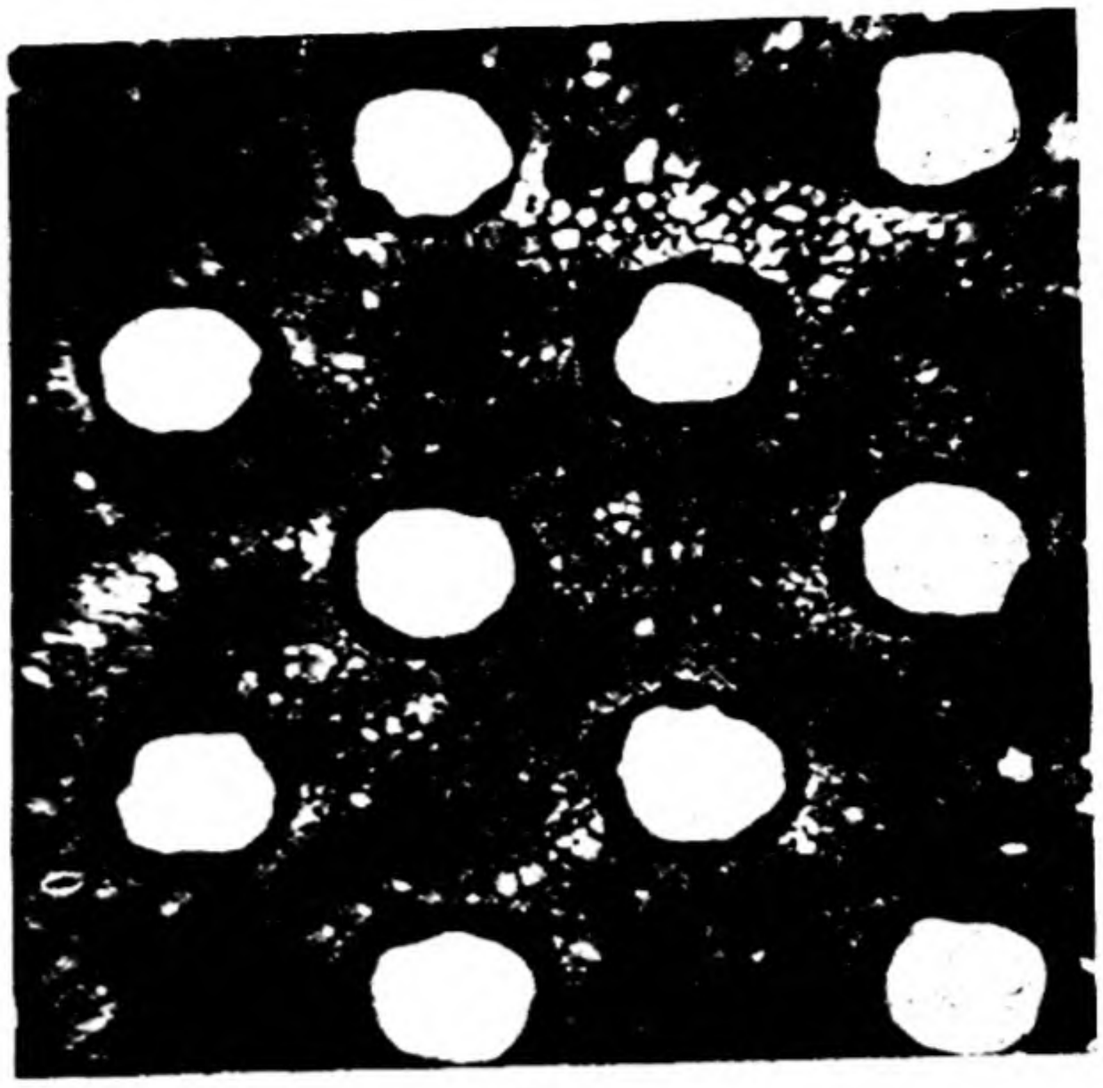
The previous figures showed the characteristics of halftone dots in the various printing presses under favorable conditions. In actual commercial printing conditions are not always favorable, and a more pronounced dot distortion may occur, leading to loss of tonal values. The influence of the paper properties has been demonstrated by Bekk.[2]

Figures VIII–9A and B show a letterpress reproduction on a smooth coated paper, characterized by a smoothness value of 1589 seconds as measured with the Bekk smoothness tester. The individual as well as the merged dots show the characteristic sharp contours and irregular color density of typography. Figure VIII–9C shows the same halftone plate reproduction on a calendered paper of a 362-

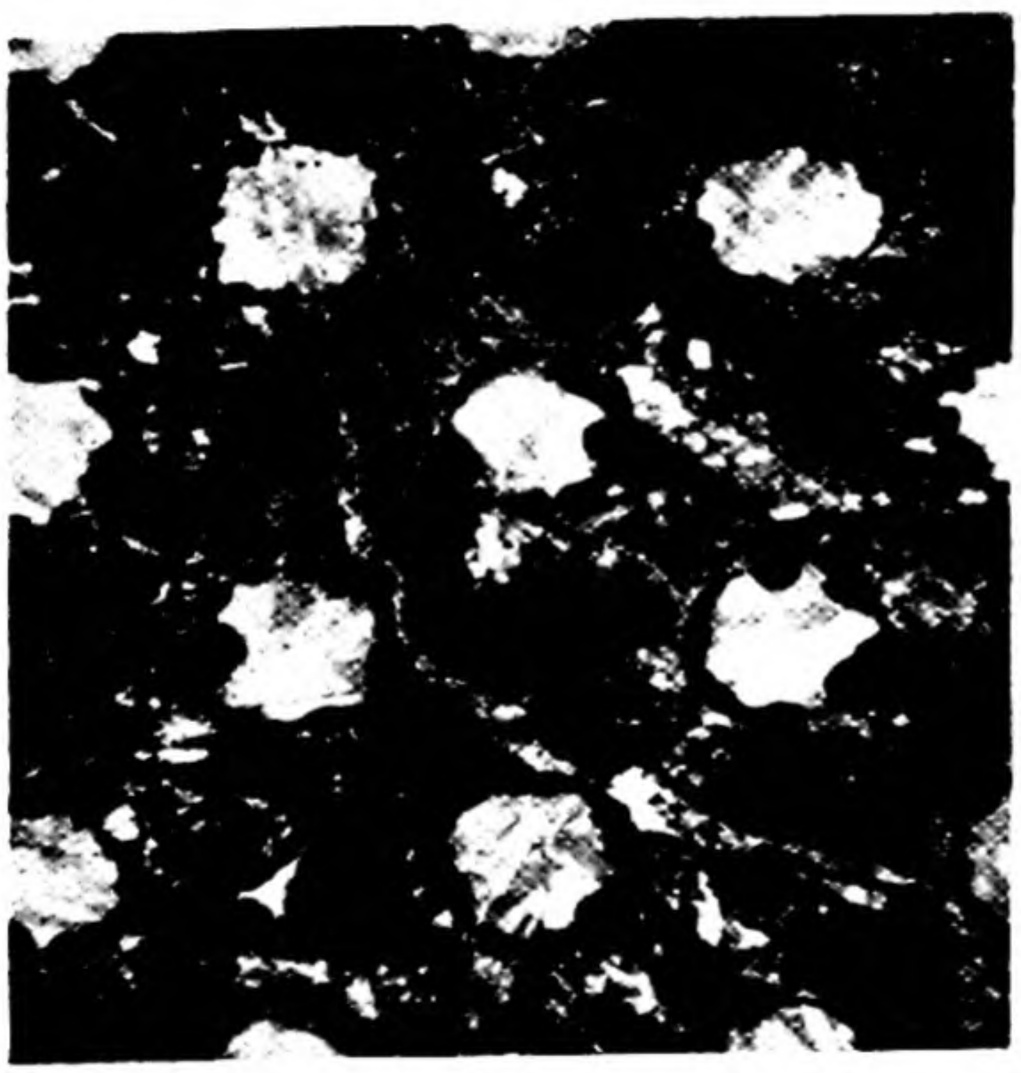
[2] J. Bekk, *What the Printing Press Demands of Paper*, School of Printing, London, 1935. Figure 9 courtesy J. Bekk.



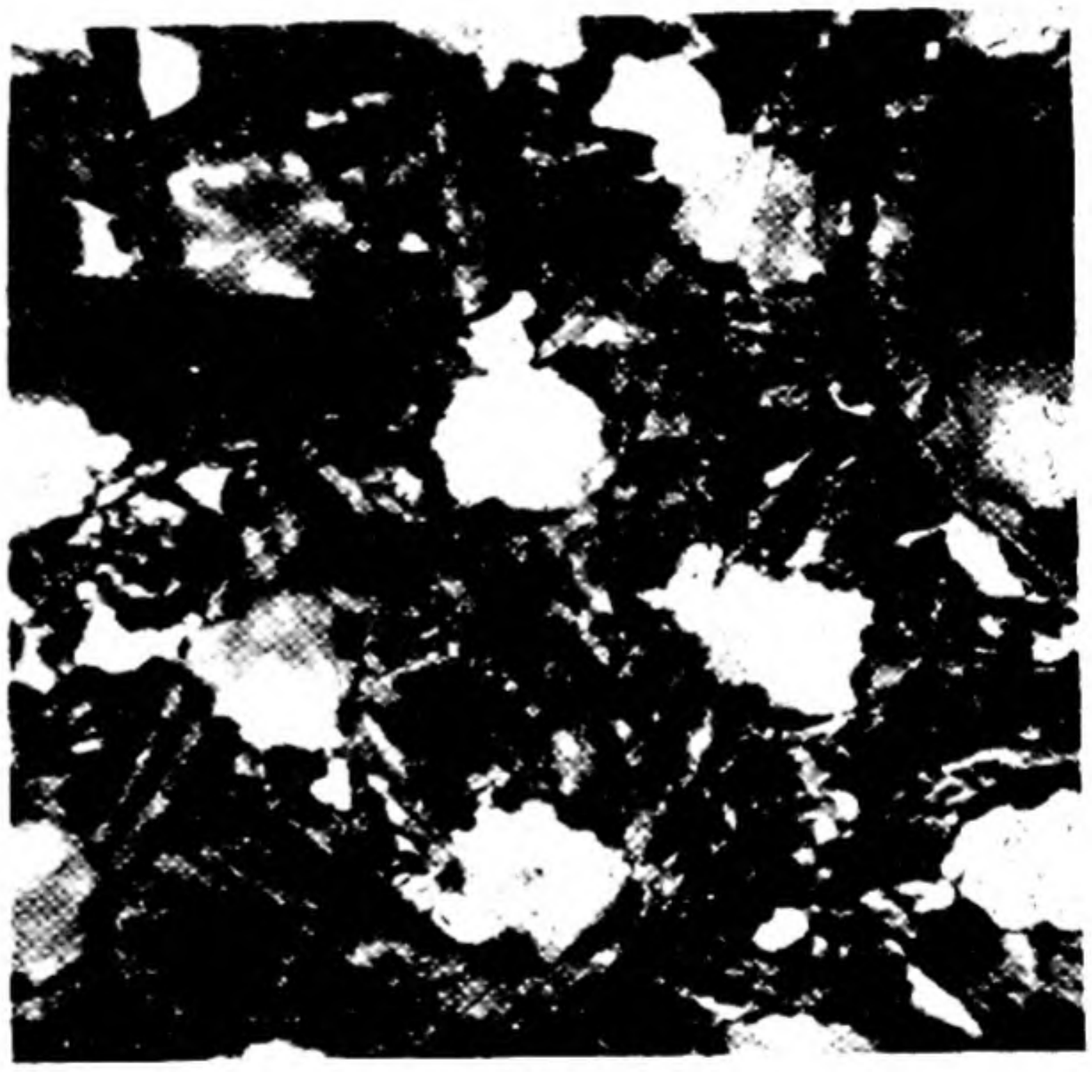
A



B



C



D

Figure VIII-9. Typographic halftone reproductions on different stocks with magnification 88×: (A) and (B) coated Bekk smoothness 1589 seconds; (C) calendered, Bekk smoothness 362 seconds; (D) news, Bekk smoothness 66 seconds.[2]

second smoothness, and Figure VIII–9D shows, in addition, the reproduction on a news stock with a smoothness of 66 seconds. It is clearly demonstrated in the photomicrographs that the rougher the paper, the more irregular is the halftone contour. The printing pressure apparently displaces the ink into the nearest recesses, follow-

ing the often irregular paper pattern. Therefore, with smooth paper the ink is uniformly "squeezed out" at the periphery of the dot, resulting in a "doughnut" effect, but with sharp contours, leading to a sharp reproduction. On rough paper, however, the sharpness of contours is largely lost, causing a marked reduction of the fineness of detail in the reproduction. The increased loss of uniformity of coverage causes an increased limitation of the gradation of color hue.

The offset lithographic process appears to be much more tolerant than the letterpress process in its requirements of smoothness of the paper stock. In the first place, even under the most favorable conditions, the offset halftone dot has a somewhat diffuse contour. Changes due to paper irregularities are therefore not of great significance. Secondly, the thickness of the offset film (1–2 microns) is roughly only one-half the thickness of the film used in the letterpress printing and is thus less likely to be displaced by the printing pressure. Thirdly, the more viscous inks used in offset lithography have a much greater resistance to deformation than the more fluid letterpress inks. Finally, the pressure on the paper is exerted by a resilient blanket and is therefore uniform, in contrast to the localized pressure in typography. For these reasons, the quality of reproduction in offset lithography is much less adversely influenced by a rougher paper than in typographic printing, a factor largely responsible for the success of offset lithography.

In the photogravure process also, a smooth paper favors the formation of sharper dot contours, while a rough stock tends to increase the faulty definition of the dots inherent in the process. Yet, as in offset printing, as a result of the inherent lack of sharp dot contours, even under unfavorable conditions the photogravure reproduction is not as adversely influenced by paper roughness as letterpress reproductions.

Softness of a paper is its quality of becoming smooth under pressure. Because a soft stock has a tendency to become smoother when being printed, a rough but soft paper will generally yield a better reproduction than a rough, hard paper.

C. CROSS-SECTIONAL PHOTOMICROSCOPY

While the photomicrography of halftone dots throws light on the properties of the printed reproductions in the different printing

processes, the microscopic observation of cross sections of prints permits a better understanding of the interaction of ink and paper.

In the cross-sectional technique the specimen is prepared by cutting sectors from prints at right angles to the surface of the paper. The sections are usually 20–30 microns thick and show enough transparency to allow microscopic observation by transmitted light. The specimen must be held rigidly when cut. This is usually done by embedding it in a soft, solid material such as elder pith. A more convenient embedding medium such as a high-melting paraffin wax has a tendency to soften and even dissolve printed films or to extract parts from the films. This difficulty may be overcome by wrapping the sample in moisture-proof cellophane before embedding it in the paraffin wax. A print provided with a cellophane protective wrap is repeatedly dipped in molten paraffin wax, thus building up a multitude of wax layers. After cooling, the specimen is mounted on the stage of a microtome, which may be of the sledge or the rotary type. The cut is freed from the cellophane wrap by means of a needle and is carefully mounted.

The cross sections disclose the character of the film and the location of the pigment. Figure VIII–10 shows a cross section of a solid on a typographic print at a 40× magnification, and Figure VIII–11 shows a halftone reproduction in letterpress, both on an absorbent paper stock.[2a] It may be seen that in both cases the pigment penetrates into the superficial paper layers. Figure VIII–12 shows a cross section of a halftone reproduction in offset lithography at 40×, indicating a relatively thin ink film. Figure VIII–13 shows a photogravure cross section at 40×. Regular patches of ink are visible, indicating that the ink penetrates into the paper according to the pattern of the photogravure screen.

Figure VIII–14 shows a letterpress cross section on a nonabsorbent machine-finished stock.[3] The ink film appears to have penetrated slightly, but is mostly found on the paper surface. Figure VIII–15 shows a cross section of a letterpress reproduction on coated stock. It is clearly seen that the ink penetrates into the clay coating, forming a smooth thin film. The body stock is entirely free from pigment, and the printing characteristics of the paper appear to be dependent predominantly upon the properties of the coating.

[2a] Figures 10–13 courtesy London School of Printing.
[3] Figures 14–19 courtesy Interchemical Corporation.

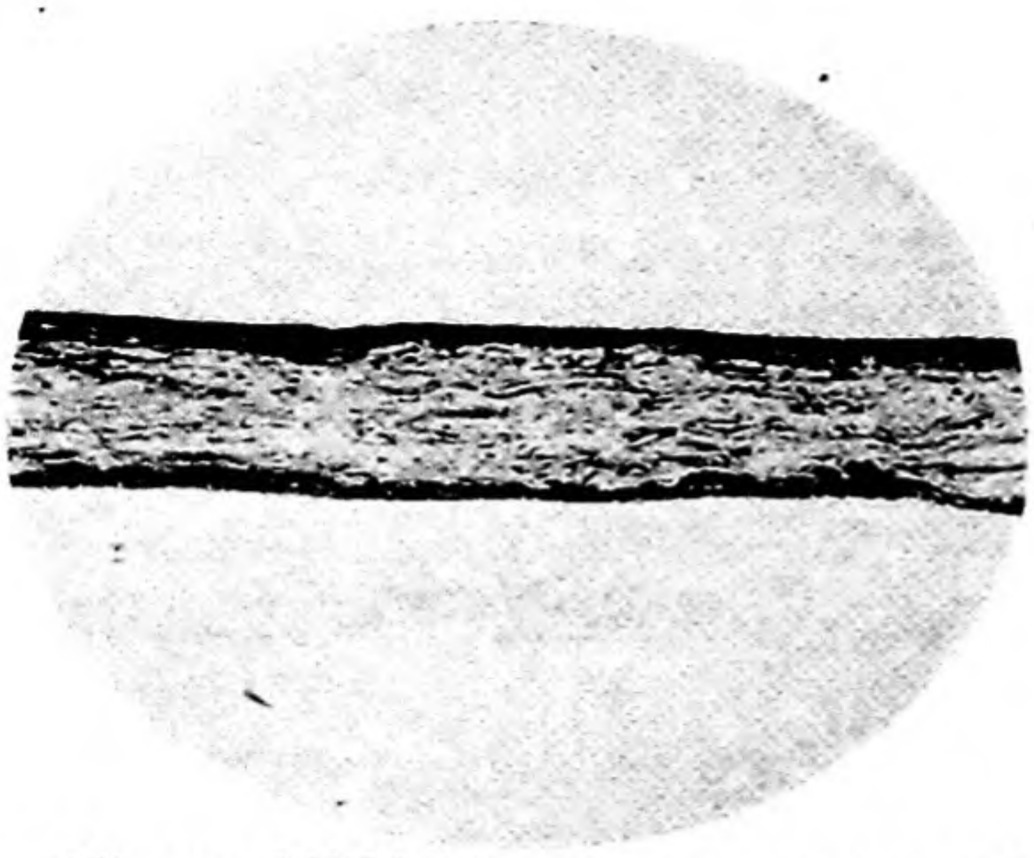


Figure VIII-10. Cross section of typography, solid, on absorbent stock. Magnification 40 ×.[2a]

Figure VIII-11. Cross section of typography, halftone, on absorbent stock. Magnification 40 ×.[2a]

Figure VIII-12. Cross section of offset lithography, on litho stock. Magnification 40 ×.[2a]

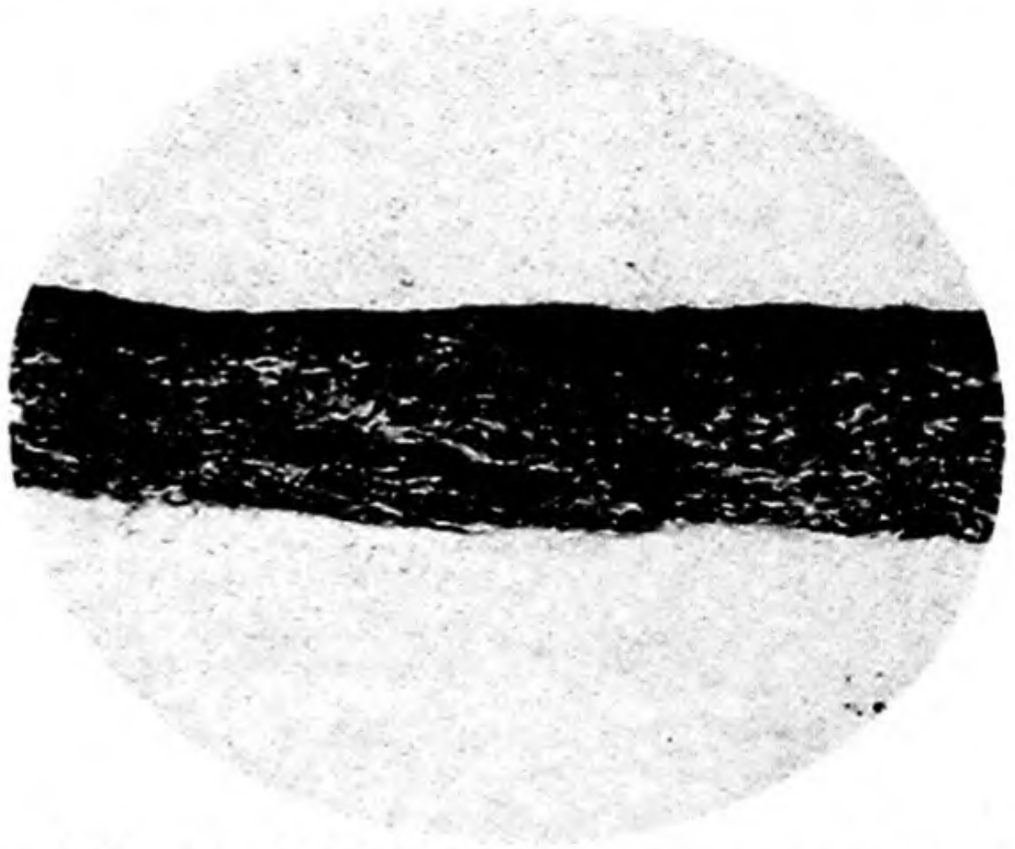


Figure VIII-13. Cross section of photogravure, solid, on roto stock. Magnification 40 ×.[2a]

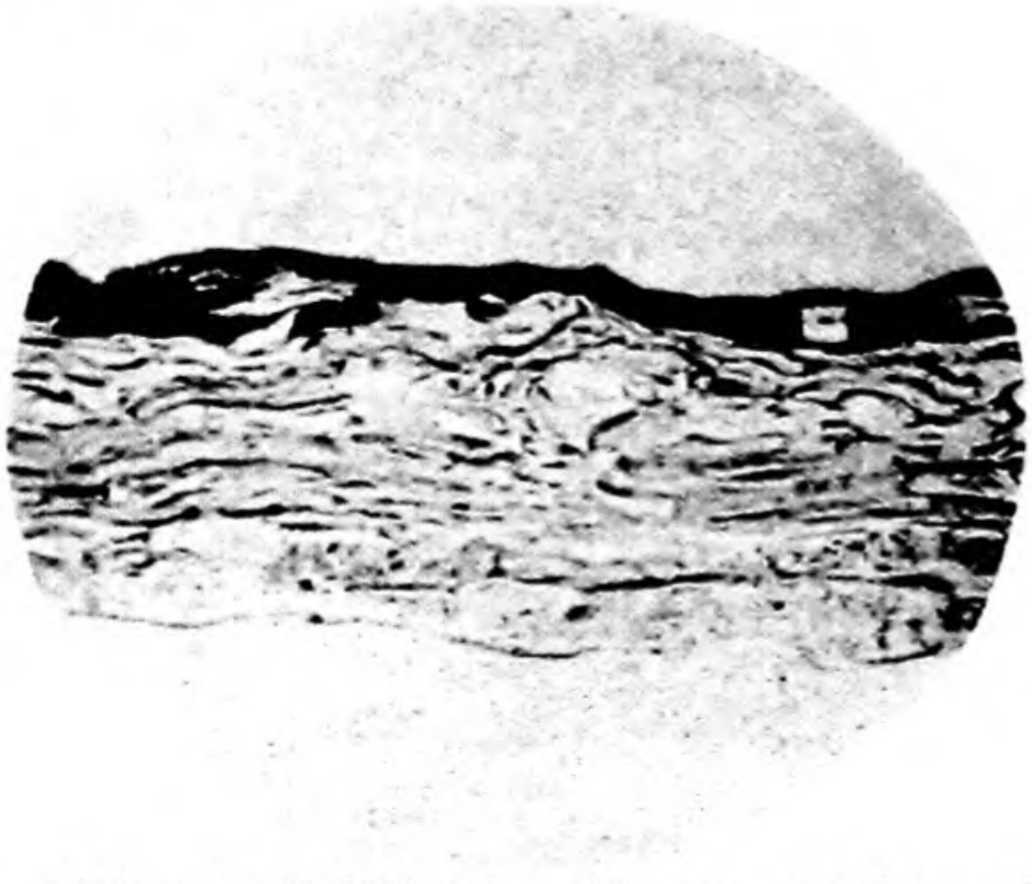


Figure VIII-14. Cross section of typography, machine-finished stock. Magnification 350 ×.[3]

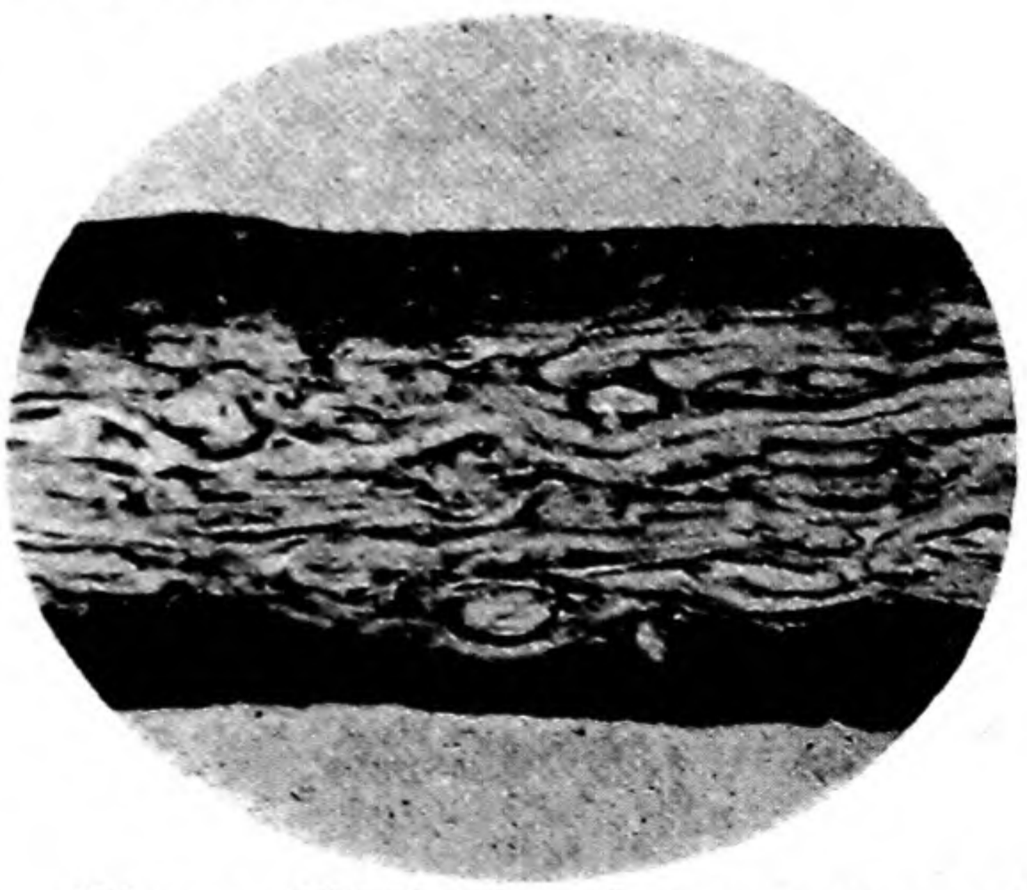


Figure VIII-15. Cross section of typography on coated stock. Magnification 245 ×.[3]

Figure VIII–16 shows a cross section of normally printed newsprint. The open structure is clearly visible, and the penetration of the pigment, without protective film on top, is noticeable. Figure

Figure VIII-16. Cross section of newspaper, normal impression. Magnification 400 ×.[3]

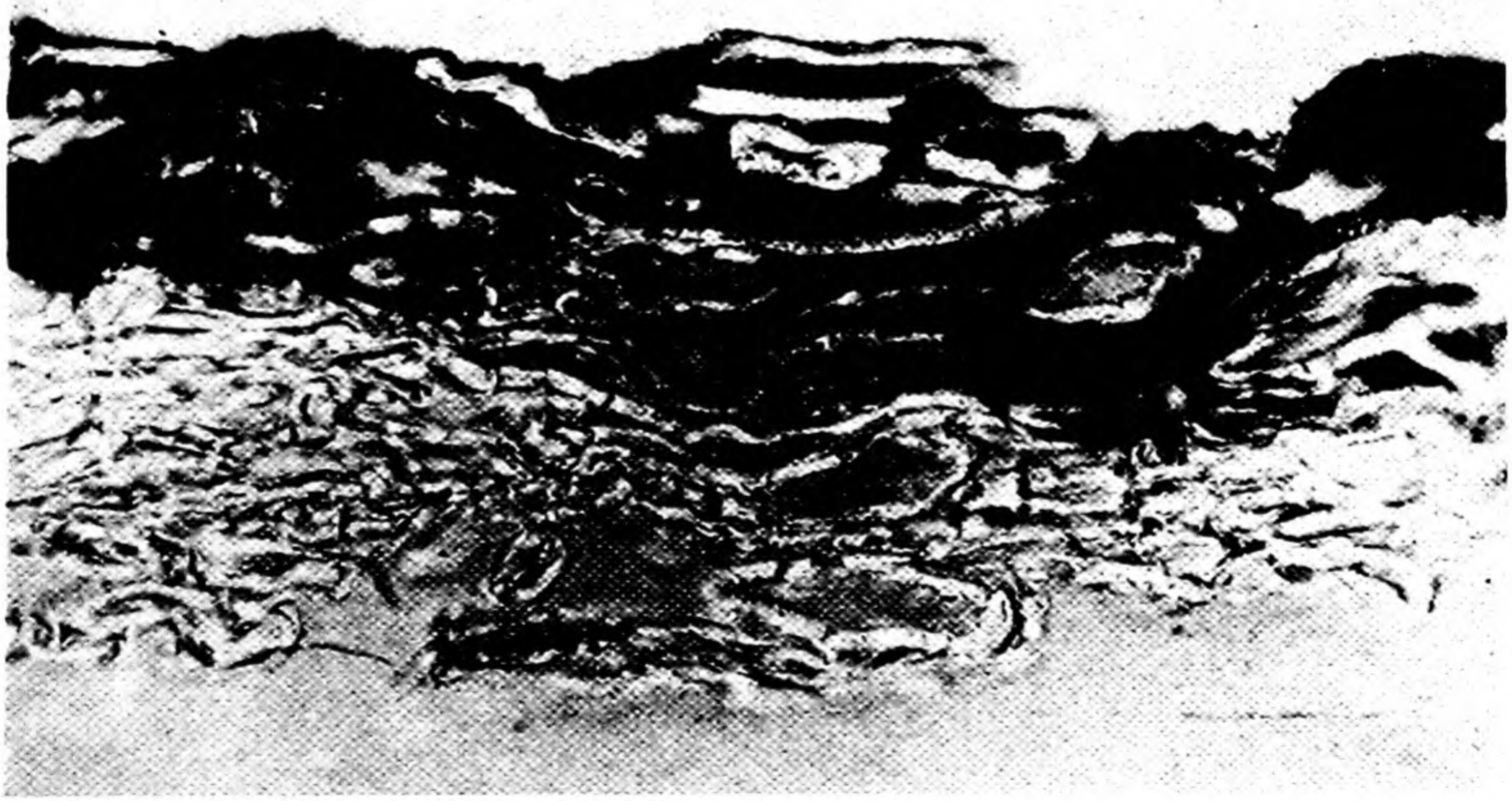


Figure VIII-17. Cross section of newspaper, heavy impression and excess of ink. Magnification 350 ×.[3]

VIII–17 shows a cross section of heavily printed newsprint, indicating a very marked penetration of pigment into the stock. Figure VIII–18 shows newsprint printed with coldset ink. Here the ink does not

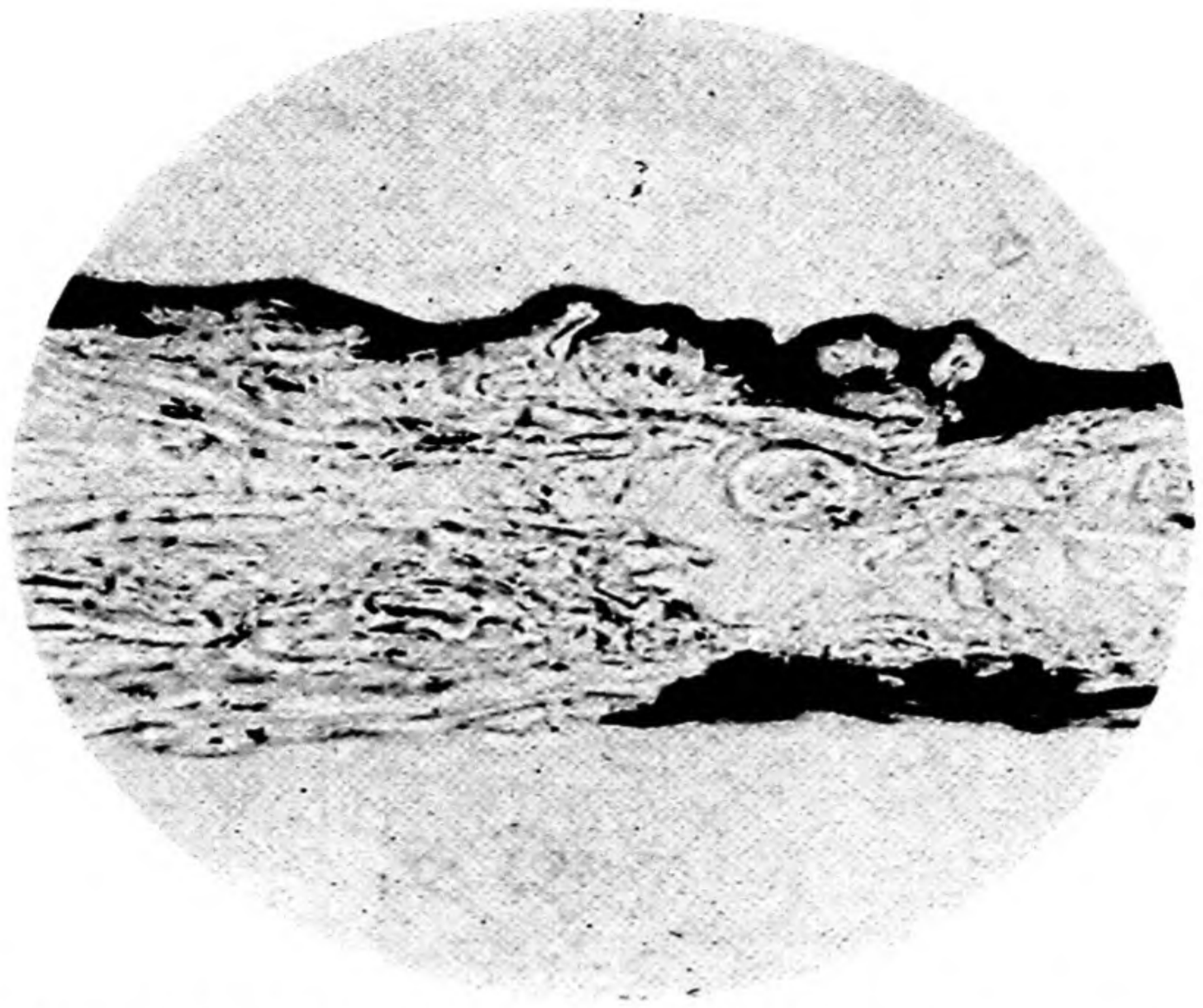


Figure VIII-18. Cross section of newspaper printed with coldset ink. Magnification 250 ×.[3]

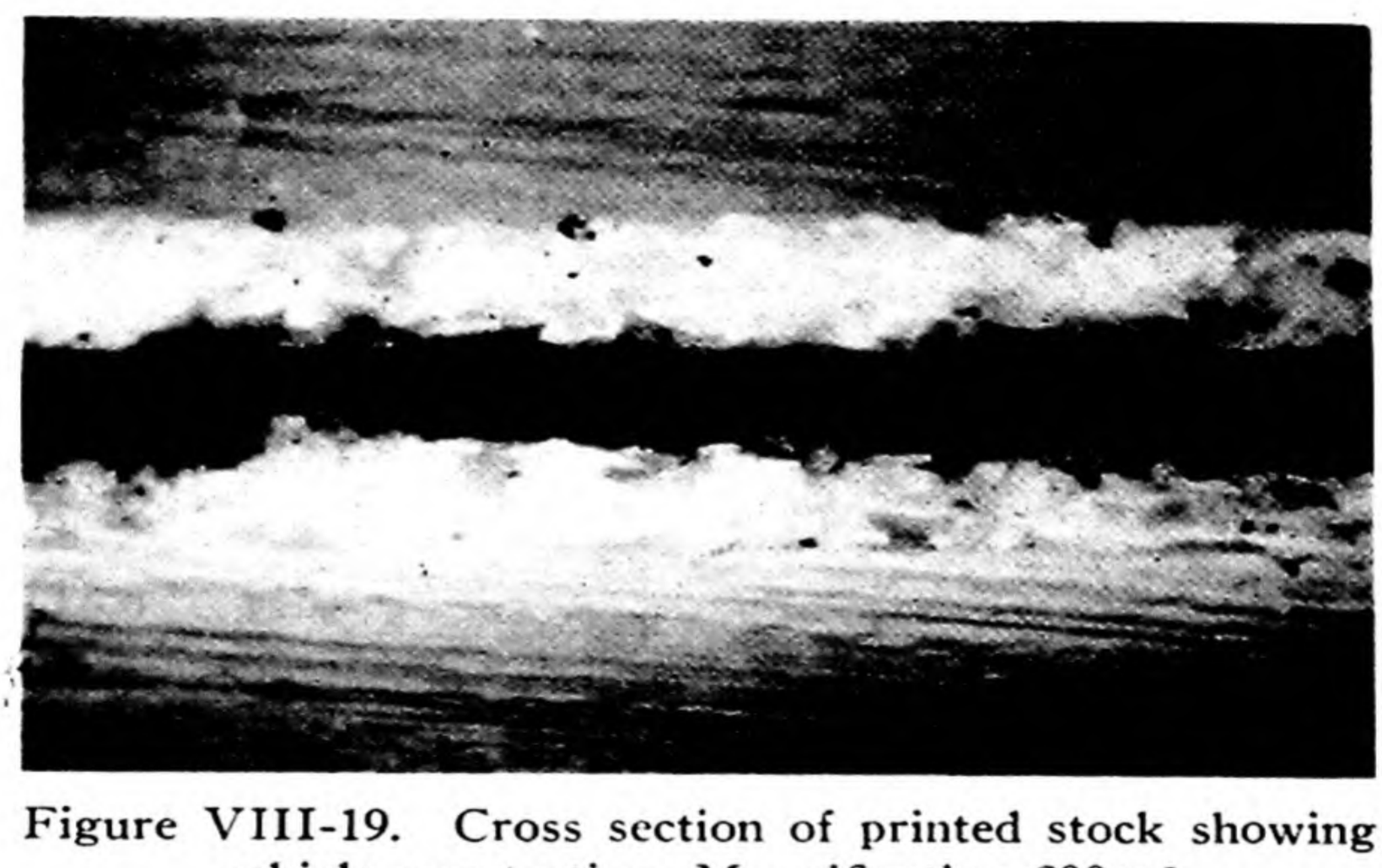


Figure VIII-19. Cross section of printed stock showing vehicle penetration. Magnification 200 ×.[3]

penetrate deeply into the stock, but remains on the paper surface. This fact, no doubt, is primarily responsible for the improved quality of coldset reproductions.

The cross-sectional technique is very useful in studying the

failures of prints. Too much ink or lack of ink, excessive penetration, and lack or excess of pressure usually will become visible in a cross section of the print. Thus, the cross section often reveals the conditions prevailing during the production of the print and forms a valuable contribution to print evaluation.

Although the location of the pigments in the printed paper are clearly observed in the cross section, the described technique does not reveal the extent of vehicle penetration. There are indications that a vehicle penetrates throughout the entire paper thickness within a few hours after printing, even with comparatively heavy papers. This is easily seen from the fluorescence on the reverse side of a print under ultraviolet light exposure.

While most ink vehicles show fluorescence in ultraviolet light, the cross sections are too thin to reveal any fluorescence by microscopic examination. A novel technique, developed by Interchemical Research Laboratories, consists of microscopic observation under ultraviolet light of one end of a print embedded in a medium and held between two steel plates, revealing a cross section made manually by means of a sharp blade. Figure VIII–19 shows such a print. The pigment is not visible, but the fluorescence of the vehicle, which penetrated from each side to about one-third of the paper depth, is easily seen as a bright zone. The dark zone in the middle is the part of the paper into which no vehicle penetration took place.

Since vehicle penetration is rapid and complete within a few hours, tests made to reveal the vehicle penetration depth must be made soon after printing.

A technique used to indicate the penetration depth of a vehicle by means of a dissolved dye in the cross-sectional procedure is not satisfactory and often misleading. Actually paper chromatography takes place, the dye is absorbed by the paper fibers, and the vehicle is left to penetrate undetected.

CHAPTER IX

CONTRAST AND COVERAGE OF INK

A. CONTRAST AND COLOR STRENGTH

The film produced by printing has the essential purpose of forming a contrast with the background, the unprinted part of the sheet. In evaluating the property of the ink to form a desirable contrast it is necessary to take into account the paper as well as the conditions of printing. In addition, there is a decided difference between halftone plates and solids or line cuts.

An old-established method of determining the "color strength" of an ink by measuring its tinting strength for a given white ink must be considered misleading. Not only does this method fail to take into account the interaction of ink and paper, but also the tinting strength for a white pigment is fundamentally a different property from the contrast of a print. Moreover, in the mixing process of determining tinting strength additional dispersion of pigments or dyes cannot be avoided. The presence of surface-active agents in the ink sometimes prevents the even distribution of pigments required for a significant test. The hiding power for a checkered plate, a method justified for paints and occasionally used in inks, is equally unacceptable as being fundamentally different from a contrast.

The only correct method of determining the contrast of a print is a direct physical measurement of the brightness of the print and of the unprinted sheet. The brightness of a surface may be defined as the ratio between incident and diffusely reflected light. As standards in a brightness scale an ideally black surface, showing no reflection, is designated with a brightness 0, while a freshly made surface of magnesium oxide, which shows a complete reflection of all incident light, is designated with 1. In actual practice secondary standards are mostly used. The term blackness is sometimes introduced as denoting the opposite of brightness, or the ratio between the absorbed and incident light. It is easily seen that the total value of blackness and brightness of a surface are always equal to 1.00, which allows an easy calculation of either of the two from the other. Meas-

urements of brightness may be carried out by means of photometers. Older types of photometers require a visual comparison with standards by means of optical wedges allowing a variable light absorption. Newer photoelectric instruments permit a direct measurement of the brightness of a surface in terms of galvanometer scale deflections.

Contrast may be defined as the difference in brightness of printed solid and paper expressed in terms of the paper brightness. Where measurements are made on prints which are all printed on the same paper, it is convenient to use the brightness of the print, or its blackness, instead of the contrast. Comparing directly the brightness or blackness of prints made on different backgrounds, however, leads to an inaccurate contrast evaluation.

B. CONTRASTS IN SOLID PRINTS

To evaluate the contrast properties of a given printing ink on a given paper, numerical values for the contrast for different amounts of ink printed on the paper must be obtained. The simplest and most accurate method of determining the exact thickness of an ink film is the gravimetric method developed by Julius Bekk[1] in his procedure for measuring contrasts. Bekk's method consists essentially of making a multitude of prints of varying film thickness from a polished steel shell held in place by clips or by an electromagnet. The plate is accurately weighed on an analytical balance, after inking and again after printing. The difference in weight is the amount of ink transferred to the paper. Direct weighing of the paper is only practicable when the pressroom has a constant temperature and humidity and the paper has been brought into humidity equilibrium with the atmosphere of the room.

Another method, involving tracers, has been developed by Buchdahl and Pohlglase.[2] The incorporation of a dye, extracted later from the print and estimated colorimetrically, yields excellent results. Another, more spectacular though not more practical or accurate method is to incorporate a radioactive tracer in the ink. Buchdahl and Pohlglase,[2] using radioactive phosphorous trichloride, measured the quantity of ink used in a print with a Geiger-Müller counter, after calibration, however, by the gravimetric method.

[1] J. Bekk, *Deut. Drucker, 38,* 1 (November, 1931).
[2] R. Buchdahl and M. F. Pohlglase, *Paper Trade J., 121,* 3 (1945).

Figure IX–1 represents a series of curves obtained by printing a black news ink on different types of stock. By far the highest blackness, for equal quantities of ink deposited, is obtained on a smooth nonabsorbing surface, such as cellophane. For example, blackness of 91 per cent is reached with 0.92 g. of ink per m.^{2} on cellophane (C), with 2.05 g. per m.^{2} on bond paper (B), and with 2.57 g. per m.^{2} for news stock (A). The characteristics of the curves show rapid saturation appears upon increasing the quantity of ink deposited. On a news stock, to increase the blackness from 91 to 93 per cent the quantity of ink required must be increased from 25.7 to 34.5 g. per m.^{2}, an

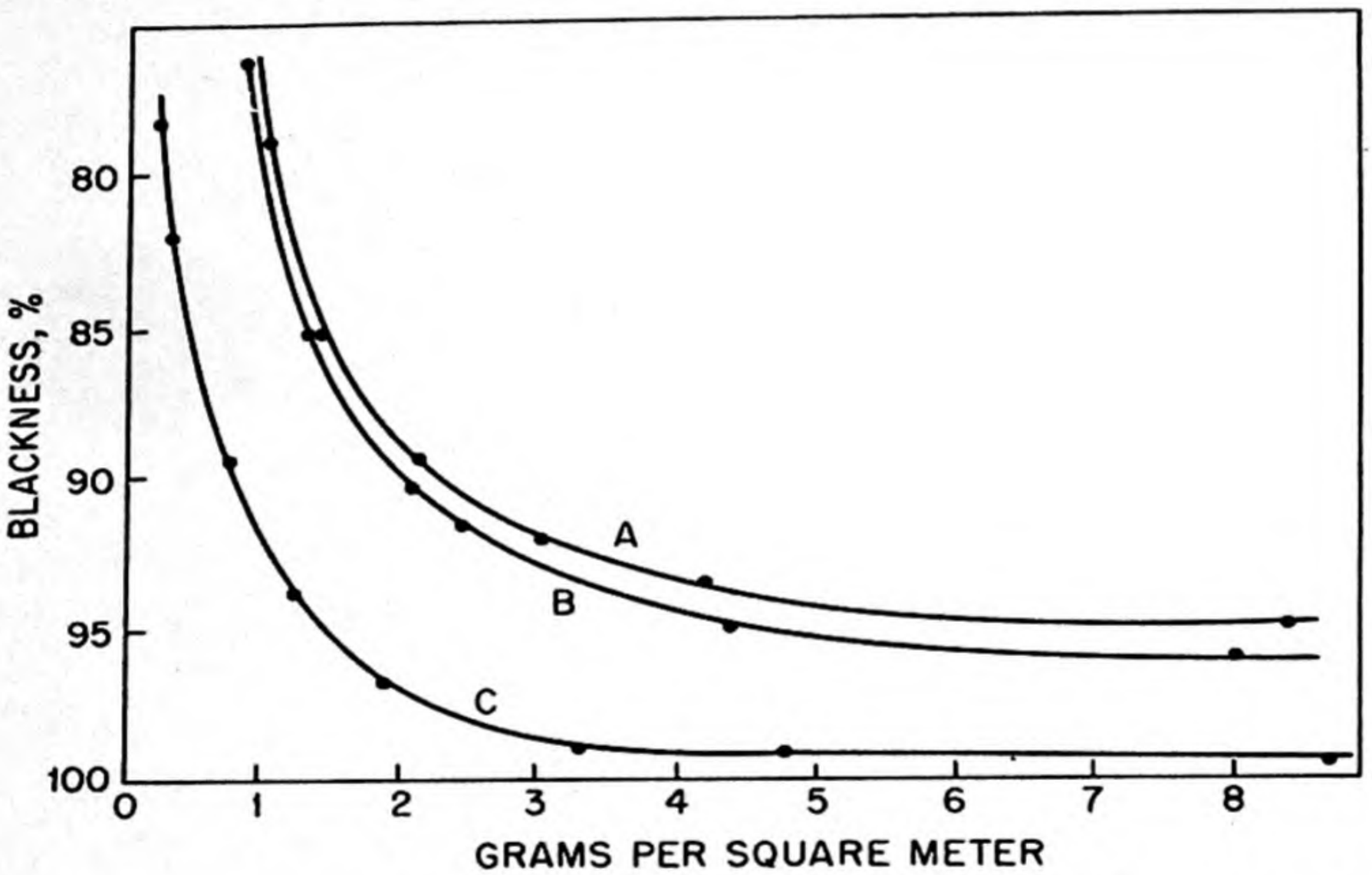


Figure IX-1. Variation of blackness of an ink on different surfaces.

increase of 34 per cent. Consequently, it appears that excess of ink, apart from causing difficulties in drying and leading to offset, is a very uneconomical means of increasing the blackness of a print.

Zettlemoyer and co-workers[3] emphasized the importance of the ultimate blackness, the highest blackness obtainable in a given paper-ink combination, representing a saturation value which is asymptotically reached in the graph. From the data it appears that the smoother and the less absorbent the paper, the greater the ultimate blackness of a given ink. The same authors found that, by plotting the logarithm of the blackness against the quantity of ink deposited on the paper,

[3] A. C. Zettlemoyer, C. G. Eckhart, and W. C. Walker, *Am. Ink Maker*, *27* (9), 23 (1949).

the data fit a straight line fairly well in a very limited, though particularly important range. An attempt, however, to establish a theoretical foundation for this relationship is probably premature. It seems that the empirical limited linear relationship does not have a fundamental significance, but it may be used advantageously for interpolation of data. Ink "mileage" may be estimated from the graphs by establishing the ink required for the desired blackness. For newspaper printing usually a blackness of 91–92 per cent appears to be satisfactory. For magazines a somewhat higher blackness (93–94 per cent) is usually obtained.

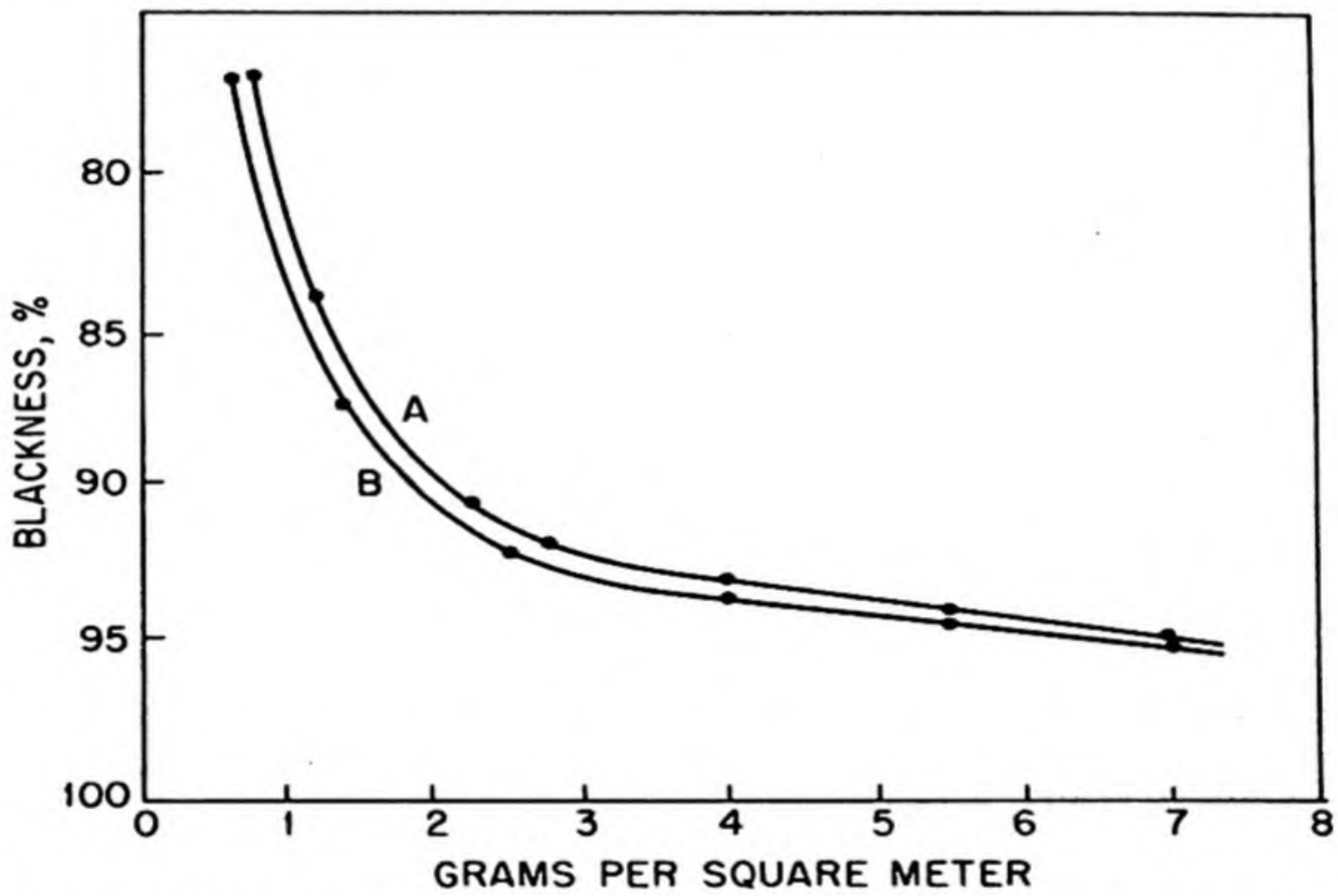


Figure IX-2. Blackness curve for felt side (*A*) and wire side (*B*) of the same stock.

The sensitivity of ink "mileage" to changes in a paper surface is demonstrated in Figure IX–2, showing the differences in blackness for the felt and wire sides of a news stock. The rough felt side needs more ink than the smoother wire side to produce the same blackness. It is easily seen that by depositing an ink film on a rough paper the "hills" will receive most of the ink while the "valleys" remain relatively free. This phenomenon may be observed directly with the aid of a stereoscopic microscope. Only by depositing a very heavy ink film on a rough stock is a better coverage obtained. A rough stock will therefore require much more ink than a smoother stock. A

rough but soft paper, which is smoothed under the printing pressure, behaves more or less as a smooth stock.

The above indicated method of evaluating contrast, with some modification, is applicable to colored prints. While it is desirable to establish a complete spectrophotogram for the entire visible range of light reflected from the print, a fairly satisfactory result is obtained by the use of a set of color filters with a narrow range of transmitted

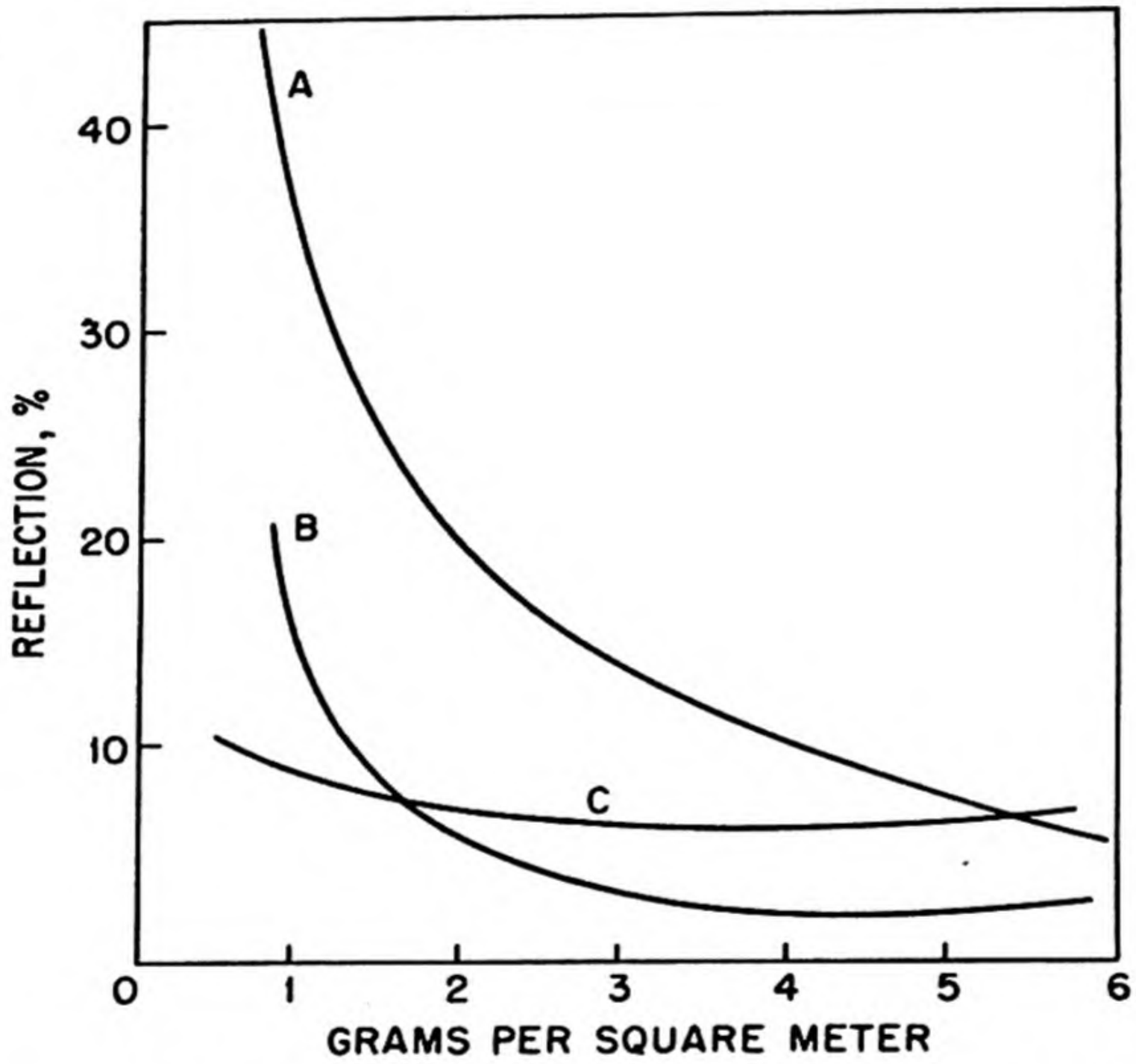


Figure IX-3. Brightness curves for a red ink: (*A*) blue reflection values; (*B*) green reflection values; (*C*) red-orange reflection values, one-tenth of actual value.

light in conjunction with a brightness tester. Figure IX–3 shows the brightness curves of a red ink, measured by Bekk[4] with the aid of three filters, a blue, an orange-red, and a green. For the real contrast the complementary color, in this case green, is the determining factor. It is generally sufficient, therefore, to measure the brightness of a colored ink by passing the light through a filter which has a color transmission range roughly complementary to the color of the print. The conclusions which may be drawn from such a curve are

[4] J. Bekk, *Deut. Drucker, 38,* 1 (November, 1931).

completely analogous to those made from the direct brightness measurements with blacks.

When lighter shades are measured or when the brightness of white paper stocks is determined, the use of a green filter is recommended. This is done because the light used often has a considerable intensity in the ultraviolet range, to which the photocell, but not the eye, is sensitive, and which is reflected by the bright surfaces. Since the human eye has a maximum sensitivity in the green, in this case the use of a green filter is recommended, to be more closely in line with the eye sensitivity.

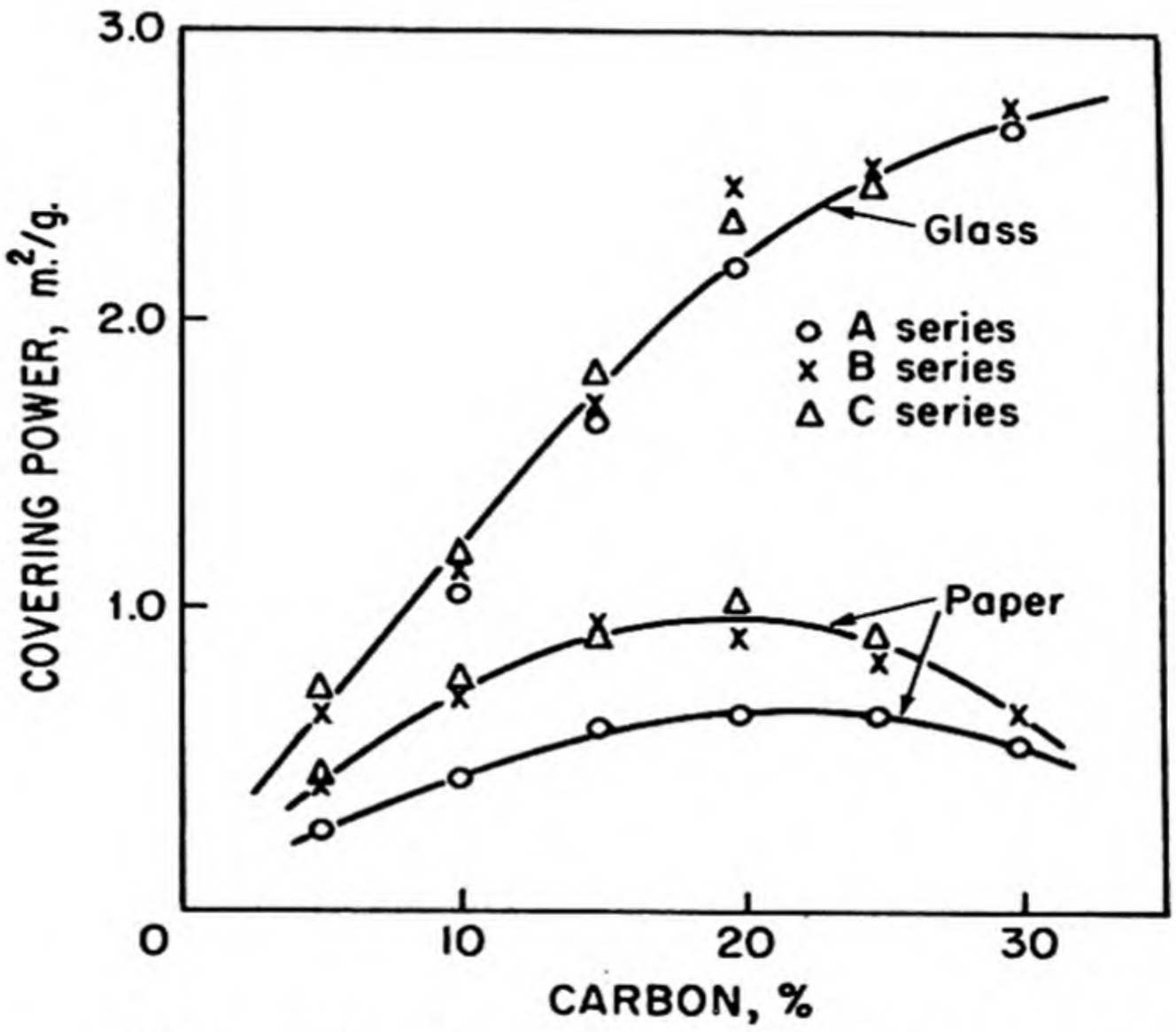


Figure IX-4. Covering power and ink composition.[5]

Mill and Colquhoun[5] studied the influence of ink composition upon mileage. They prepared inks consisting of a mineral oil and carbon black and varied the oil viscosity as well as the pigment concentration. Three oils were used, of a viscosity 2.5 poises (A), 37 poises (B), and 62 poises (C) at 20°C. The carbon black content was varied from 5–30 per cent by weight. As covering power the number of grams per square meter requiring an 80 per cent blackness was taken. It was found, as indicated in Figure IX–4, that on glass there is no difference between inks made with different vehicles, but

[5] C. C. Mill and J. W. Colquhoun, *Am. Ink Maker, 20* (2), 29 (1942).

a steady, nearly linear increase of blackness with pigment concentration was observed. On the other hand, on newsprint the inks with the least penetrating vehicle showed the highest mileage. It was noted that while initially the blackness increases with the percentage of carbon black, a maximum was reached at about 20 per cent black, after which there was a decline. This decline must be ascribed to the poor rheological characteristics of the heavier inks which did not show a proper transfer but piled up on the plate.

From these tests it is apparent that increased pigment content does not automatically lead to an increased blackness but that rheological ink characteristics are also of importance. Uneven films, of poor "laying" qualities, and unsatisfactory ink transfer decrease the mileage of an ink. It is equally apparent that inks with identical pigment contents do not necessarily have the same mileage. At equal penetration power of the vehicle the ink with the more satisfactory rheological properties will show the better mileage, whereas a more penetrating ink will have a decreased mileage. Excess penetration will result in a "waste" of coloring power, since coloring material which has penetrated deeply into the stock will not be effective as coloring agent on the paper surface and will not contribute much to the blackness of the sheet. On the contrary, such deeply penetrating color bodies will cause an increased show-through, a very undesirable phenomenon.

C. CONTRAST AND COVERAGE IN HALFTONES

Although the importance of reproducing type matter and solids as a densely printed black cannot be underestimated in publication printing, it must be stated that the main effort is usually directed toward obtaining a satisfactory halftone reproduction. Good publication printing is generally associated with excellence acquired in halftone reproductions.

The evaluation of a halftone reproduction has always been subjective and could not be given a numerical value. Since it is not possible to appraise a halftone reproduction in quantitative terms, it is rather difficult to evaluate the influence of the various factors determining the characteristics of the halftone. Bekk[6] has indicated a way in which these difficulties might be overcome. The method is based

[6] J. Bekk, *Svensk Papperstidn., 14,* 454 (1934); *Das Druckgewerbe, I,* 343 (1948).

on the premise that for an ideal reproduction the details are equally well distinguishable in the original as in the reproduction. Since the distinguishing of a detail depends on the contrast created, the method is basically one in which a series of contrasts of known magnitude are made on a halftone plate and reproduced on paper. The lowest contrast distinguishable in the reproduction by the human eye (threshold value) may then be determined. When the exact numerical value for the contrast in the original is known, a correlation can be made between the threshold value determined in the various prints and the actual contrast of the original.

The technique is predominantly one of creating a series of known contrasts. This was carried out by Bekk as follows. An optical wedge was prepared, nearly completely transparent on one end and absorbing most of the incident light on the other end. Such a wedge may be prepared by applying to a glass plate held at a small angle to the horizontal a heated aqueous solution of gelatin in which a black-colored dye mixture has been dissolved. The glass plate is provided with small end plates to prevent the liquid from running off the plate. After solidification of the solution the wedge is ready for use. A transparent plastic plate was then provided with a series of completely opaque broad lines by drawing on the surface heavy parallel lines of India ink 1 cm. apart. The plate was placed on top of the wedge, thus yielding the desired contrast object. A halftone plate was then made from the wedge by means of the cold enamel process. Great care was taken not to interfere manually with the photographically obtained halftone reproduction.

It was necessary to determine for each line the actual contrast on the metal plate, corresponding to the contrast for an ideal reproduction. This involved the exact determination of the ratio of dot surface area immediately adjacent to the lines to the nonprinting areas and was carried out by means of a microscopic projection of the relevant areas and the exact determination of the area of the projection by means of a planimeter. In this way it was easy to obtain contrasts from 0 to 0.50 in twenty steps, a range satisfactory for practical purposes.

A series of prints were made with the halftone plate on a proof press, using increasing quantities of ink, which were determined gravimetrically. The reproductions were examined and the number

of lines that could be distinguished in each print was determined. Since the contrast of each line was exactly known in the original, it was possible to determine directly the contrast needed to reproduce a contrast of the threshold value. At the same time the conventional blackness curve was determined.

Figure IX–5 indicates for two inks on the same stock the blackness, depending on the quantity of ink deposited (upper half) as well as the contrast (lower half). The data indicate that the threshold

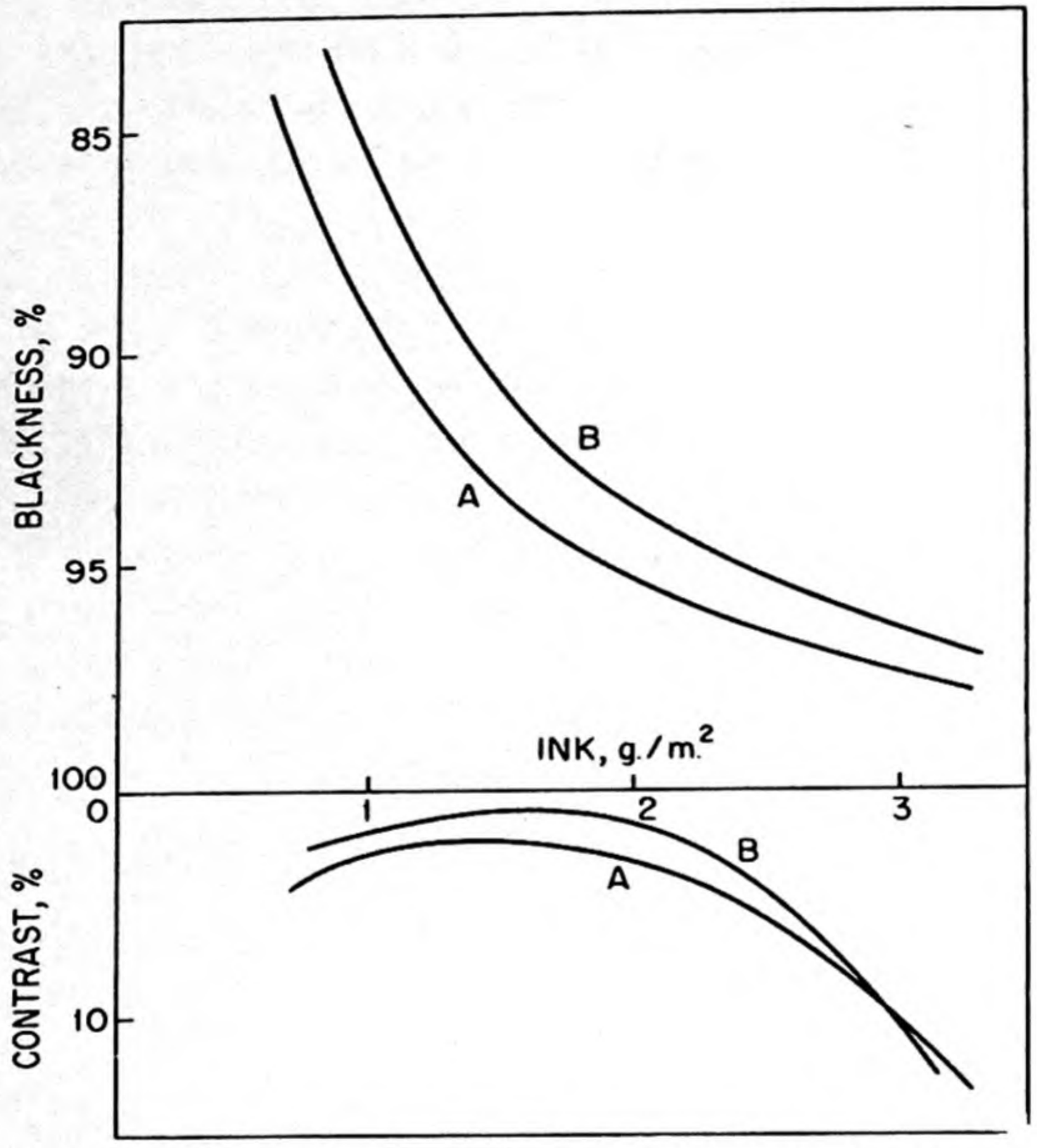


Figure IX-5. Contrast and blackness in halftones.

value of the contrast visible to the eye increases with increasing quantities of ink deposited per surface area, reaches a maximum, and declines markedly thereafter. The conventional blackness curve reaches a saturation value, but never decreases. The differences are explained by the fact that the dot formation is regulated by the amount of ink deposited. When not enough ink is available proper dots cannot be formed, while too much ink will cause excessive dot deformation, fill-in of halftones, and flooding, a deposition of ink on the nonprinting

areas. These cause a poorer reproduction and a poorer contrast. From the graph it appears that the best tone differentiation is obtained for ink B, which is distinctly superior to ink A. The maximum in the curve for ink B, requiring about 1.9 g. of ink per m.², corresponds to a blackness of 93 per cent. The maximum in the curve for ink A, requiring about 1.8 g. of ink per m.², corresponds to a blackness of 95 per cent. In actual tests with the halftone plates ink B was judged to be superior, allowing better tone differentiations, notwithstanding the greater blackness of ink A. The halftone contrast plate thus not only indicates quantitatively which of the inks has the highest tone differentiation, but it also shows the most desirable blackness and the amount of ink required. Both excess as well as deficit of ink lead to decreased tone differentiation.

The halftone contrast plate may be prepared for every size of halftone screen. Extensive measurements on news inks, however, have shown that a very flat maximum, covering a wide range, is obtained for a 60-line screen with commercial newsprint, making a quantitative evaluation of the contrast in newspaper printing difficult. This is due to the dot distortion inherent in newspaper printing, even under the most favorable conditions, resulting in comparatively poor prints. For finer screens and better paper, however, it appears that Bekk's halftone contrast plate yields excellent results and allows the quantitative evaluation of ink-paper combinations for halftone printing.

CHAPTER X

UNIFORMITY OF INK FILMS

The uniformity of a solid print is the evenness of color. A uniform print shows equality of brightness over the entire printed area. If the solid areas are uneven, they usually have a speckled, mottled, or grainy appearance. Microscopically small denser areas are surrounded by lighter borders, and the edges usually are uneven. Lack of uniformity markedly reduces the quality of a reproduction. It is usually caused by a faulty ink distribution mechanism on the press, by poor flow characteristics of the ink, or by unsatisfactory paper, lacking uniformity of formation.

Microscopic examination generally will give a fair impression of the uniformity of a print. Bekk[1] introduced an improved method, by which the print is mounted on a slowly revolving table and is photographed during the rotation with transmitted light at an enlargement. Defects in uniformity of print thus become visible as very pronounced circular variations in color density of the photograph. Examples are given in Figure X–1.

The objective numerical evaluation of uniformity is based on the measurement of brightness at a large number of spots on the print. A method used in the Pulp and Paper Research Institute of Canada is to mount the specimen on the stage of a microscope and to illuminate it highly from the side. The print is scanned with a microscope objective lens, and the brightness of the image is evaluated quantitatively by means of a projection on a photocell.

Another method is to make a photographic enlargement at a 3 × magnification using a plate with a linear relationship between optical density and the logarithm of the exposure time in the range of the densities of the print.[2] The negative is then scanned with a microdensitometer. The smallest scanning area used, necessarily larger than the limits set by the power of resolution of the human eye, was 0.02 mm.^{2}. A direct scanning by measuring the intensity of the re-

[1] J. Bekk, *Zellstoff u. Papier*, *16*, 281 (1936).
[2] R. Buchdahl, M. F. Pohlglase, and H. C. Schwalbe, *Paper Trade J.*, *122*, *18*, 41 (1946).

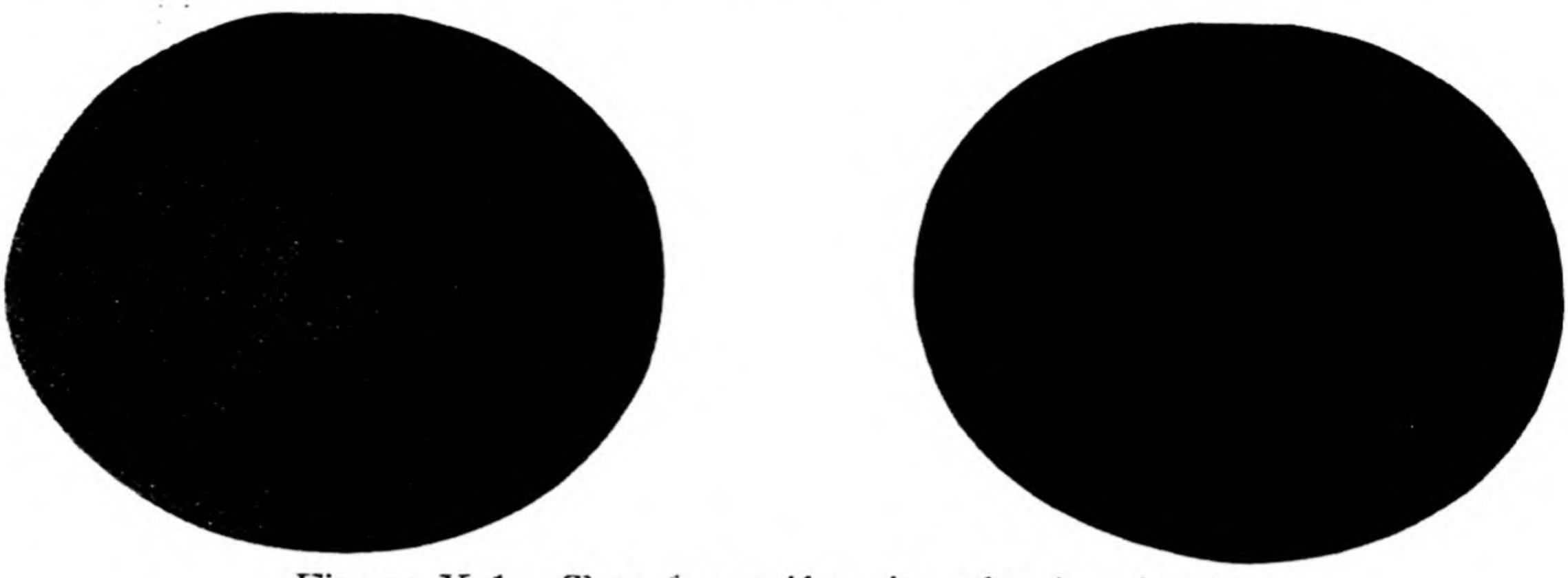


Figure X-1. Test for uniformity of color density.[1]

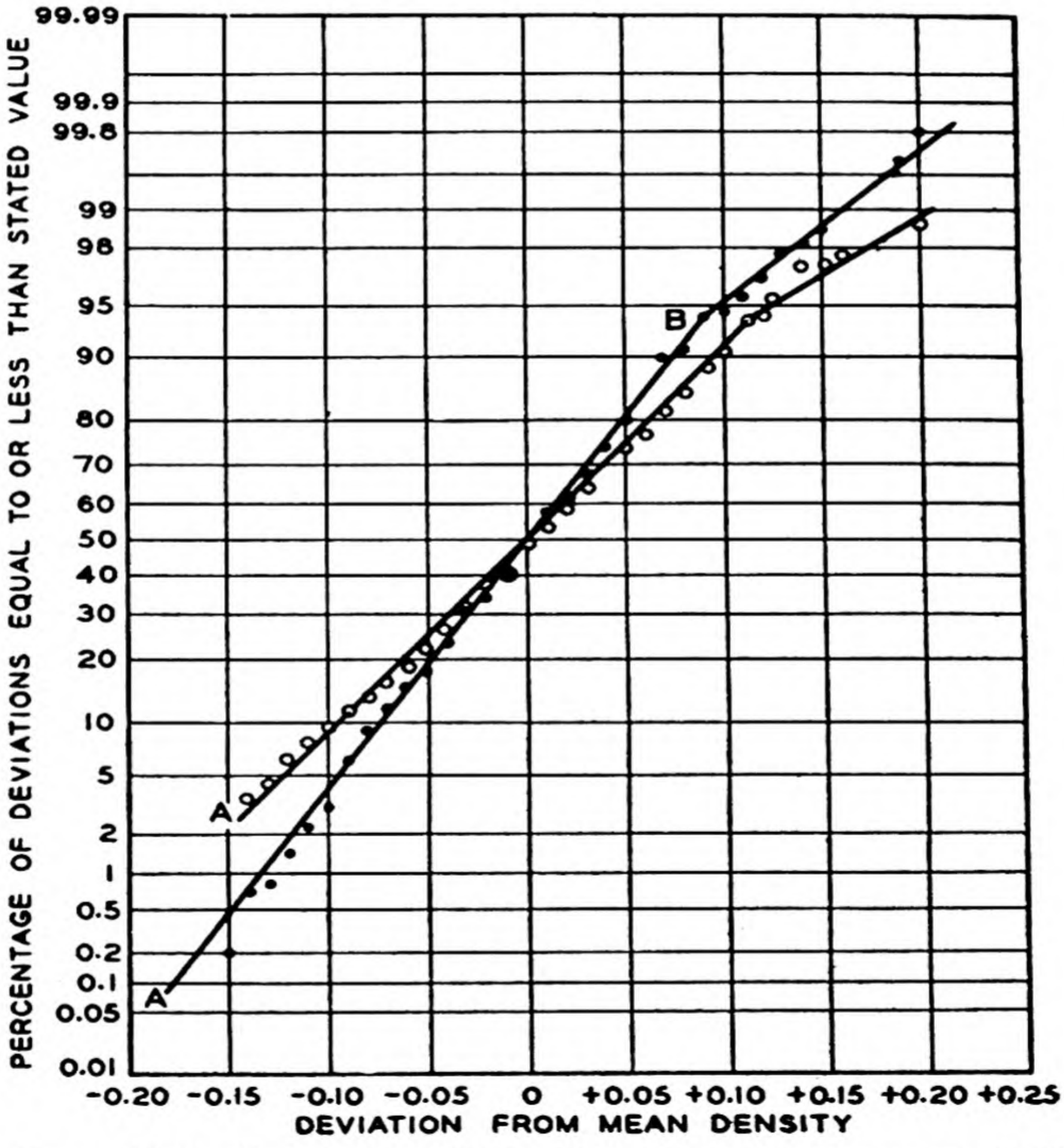


Figure X-2. Frequency distribution of density measurements.[2]

flected light is technically more difficult and might possibly be done with the aid of electron multiplier tubes.

The evaluation of the data obtained was carried out by the authors by means of a graphic representation of the frequency distribution of the densities measured in a diagram. By plotting the logarithm of the number of deviations against the square of the deviations from the mean, a "normal" distribution, following the Gaussian distribution laws, yields straight lines. Such a plot is most conveniently carried out on "probability" graph paper. Figure X–2 shows the result obtained by Buchdahl *et al.*[2] for two different prints. It may be seen that random distribution is followed up to a certain point, beyond which a sharp break occurs. It appears that the deviation from the normal distribution may be expressed in two parameters, namely, the location of the point B along the line and the slope of the line AB. The length of the line AB denotes the extent of the mottle in the ink film. The lower the point of break, the more pronounced the mottle. The magnitude of the change in slope appears to indicate the extent of bright spots.

In a series of subjective evaluation tests of prints by experts and a comparison of the results with the parameters, Buchdahl found the best correlation when equal weight was given to both parameters in the final evaluation.

CHAPTER XI

PENETRATION OF INK INTO PAPER

A. INK PENETRATION AND PAPER STRUCTURE

The phenomenon of ink penetration is of great importance in the setting of inks. Ink penetration occurs in all but the completely nonporous papers, such as glassine stock, and is more pronounced in porous stocks. An indication of the porosity of a paper may be obtained by means of the air porosity test. Table XI–1 gives the air porosity of different papers, expressed as the number of seconds required to pass 100 cm.^{3} of air at a pressure of 12.2 g. per cm.^{2} through an area of 1 in.^{2} of the paper surface, measured with the aid of the Gurley densometer.

TABLE XI–1

Air Porosity of Papers

Paper	Air porosity in Gurley seconds
Coated	1080
Machine finished	3040
News	45
English finish	76
Antique	190
Bond	360
Glassine	∞

In news inks the setting by penetration is the only method of ink drying. In nearly all other forms of ink drying the initial setting is greatly influenced by ink penetration, but the final stage of ink drying is caused by some other means, such as polymerization, oxidation, or evaporation. The printability of a paper, a quality which indicates the suitability of a stock to accept a printing ink, is connected with the speed of penetration of the ink into the stock.

B. MEASUREMENT OF INK PENETRATION SPEED

A conventional method of determining the speed of penetration of an ink into a paper is the flotation method, whereby the paper

is deposited on the ink surface or on an ink drop and the time needed for complete vehicle penetration causing uniform wetting of the reverse side is recorded. This method is rather unreliable because of the difficulties involved in determining precisely the moment of complete penetration.

Paper manufacturers have replaced inks with a test vehicle, for which castor oil is generally used. A castor oil test is adopted as a standard.[1]

Numerous investigations have been made on the subject of ink penetration. Strachan[2] recognized the influence of fiber spacing and paper sizing. Andrews[3] studied the influence of the viscosity of the penetrating oil. Larocque[4] made an extensive investigation of oil filtration through paper under pressure and studied the influence of viscosity and surface tension of the oil. The initial phase of oil absorption was deemed the most important. On the other hand, Reed[5] emphasized the significance of the saturation time.

A contribution to the study of ink penetration proper was made by Bekk,[6] who removed the excess of ink from printed stock after varying, short periods of time and marked as "penetrated" ink the difference in weight of ink quantities applied and removed. As a scientific method of investigation Bekk's penetration test fails, since the pressure exerted on the ink film by removing the ink excess between paper rollers causes ink penetration far beyond the quantity penetrating without outside pressure.

Albrecht[7] carried out a number of investigations of ink penetration with Bekk's apparatus. The results obtained suffer from the limitations of the method, and no fundamental relationships were uncovered.

Wehmhoff[8] measured the number of sheets of paper penetrated

[1] TAPPI Tentative Standard T462 n 4.3, June 1943, revised December 1943.

[2] J. Strachan, *Paper Mill, 52* (3), 24 (1929).

[3] I. H. Andrews, *Paper Trade J., 90,* 16 (1930).

[4] G. L. Larocque, *Pulp & Paper Mag. Can., 38, 77* (1937); *Paper Ind. and Paper World,* 460 (1938).

[5] E. O. Reed, *Paper Trade J., 100,* 41 (1935).

[6] J. Bekk, *Papier-Fabr., 31,* 485 (1933).

[7] J. Albrecht, *Färben-Ztg., 43,* 1011 (1938).

[8] B. L. Wehmhoff *et al.,* U. S. Government Printing Office, Tech. Bull. No. 18, 1933.

by a drop of ink in a definite period of time of at least several hours. This method is not very satisfactory.

Dodge and Tarvin[9] determined photoelectrically the change in reflection with time of a paper surface while ink was penetrating from the reverse side. They stated that the time required for a predetermined numerically expressed change in reflection is indicative of the speed of ink penetration. Although the authors had built an excellent research tool, they did not use their instrument for more fundamental investigations, nor did they report any basic relationships between ink properties and penetration speed. The main idea of the instrument described by Dodge and Tarvin was incorporated in the so-called News Penetration Tester, a commercially available instrument which basically determines only the end point or a single desired midpoint of reflection changes in a paper surface as a result of ink penetration from the reverse side.

C. FACTORS INFLUENCING INK PENETRATION

A general investigation of the factors influencing ink penetration was carried out by Voet and Brand,[10] who measured the reflection of the reverse side of the paper surface by means of a photoelectric reflectometer. In the photovolt reflectometer, in part indicated in Figure XI–1, light passes through an optical system and is cast as a parallel beam upon the surface to be measured. While the directly reflected light is thrown back through the system and dissipated, the diffusely deflected light falls upon photocell *p*. Its intensity is measured with the aid of a very sensitive galvanometer. At the start of the operation the galvanometer deflection is set, by means of a resistance in a shunt, to its maximum deflection as caused by the light reflection from the paper surface *A*, held in place by ring *B*.

Care is taken to prevent the influence of outside light sources by covering the paper with an opaque cover *C*, which is dull black inside. A definite volume of ink, sufficient to fill up the space between ring and paper, is now deposited on the paper surface, and the change in photocurrent with time is marked. The result obtained is a reflection-time curve. Figure XI–2 shows the results for inks A and B on the same stock.

[9] W. G. Dodge and C. E. Tarvin, *Paper Trade J., 100* (5), 38 (1935).
[10] A. Voet and J. S. Brand, *Paper Trade J., 122* (24), 35 (1946).

It was observed that the reflection-time curve is perfectly linear for the greater part, but near the saturation the expected change of

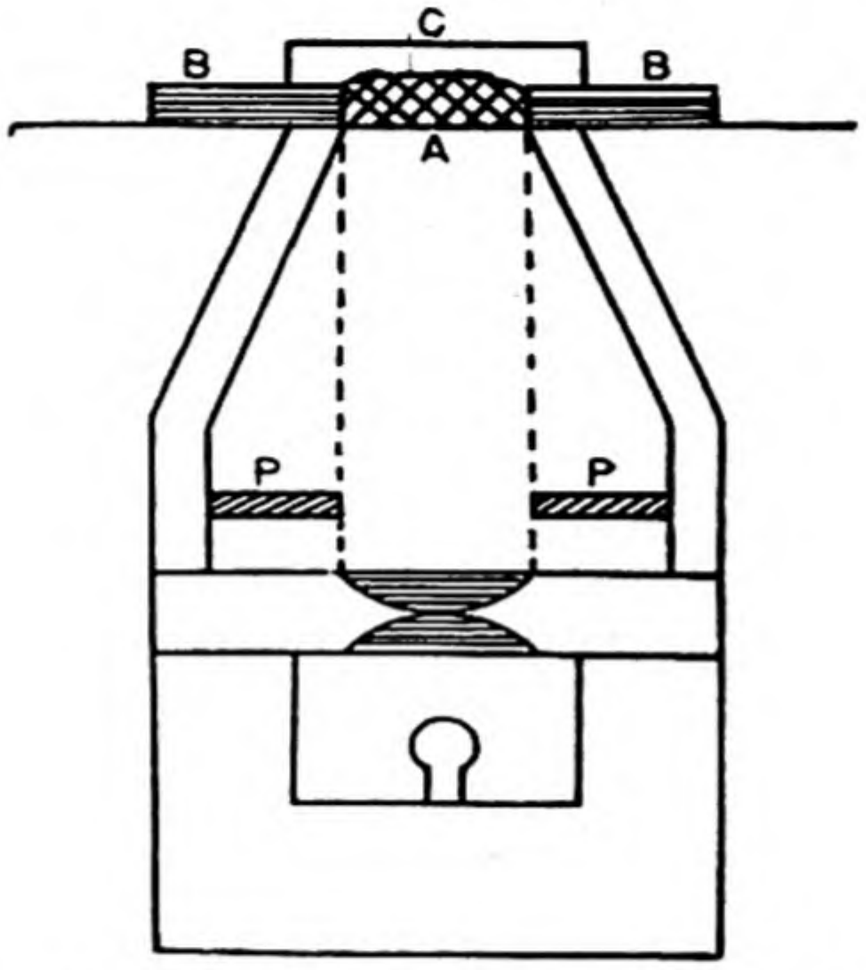


Figure XI-1. Photoelectric reflectometer.[10]

the curve was found. It is obvious therefore that the speed of penetration is constant during the main period of penetration and decreases only at the end, finally reaching a standstill period. The speed of

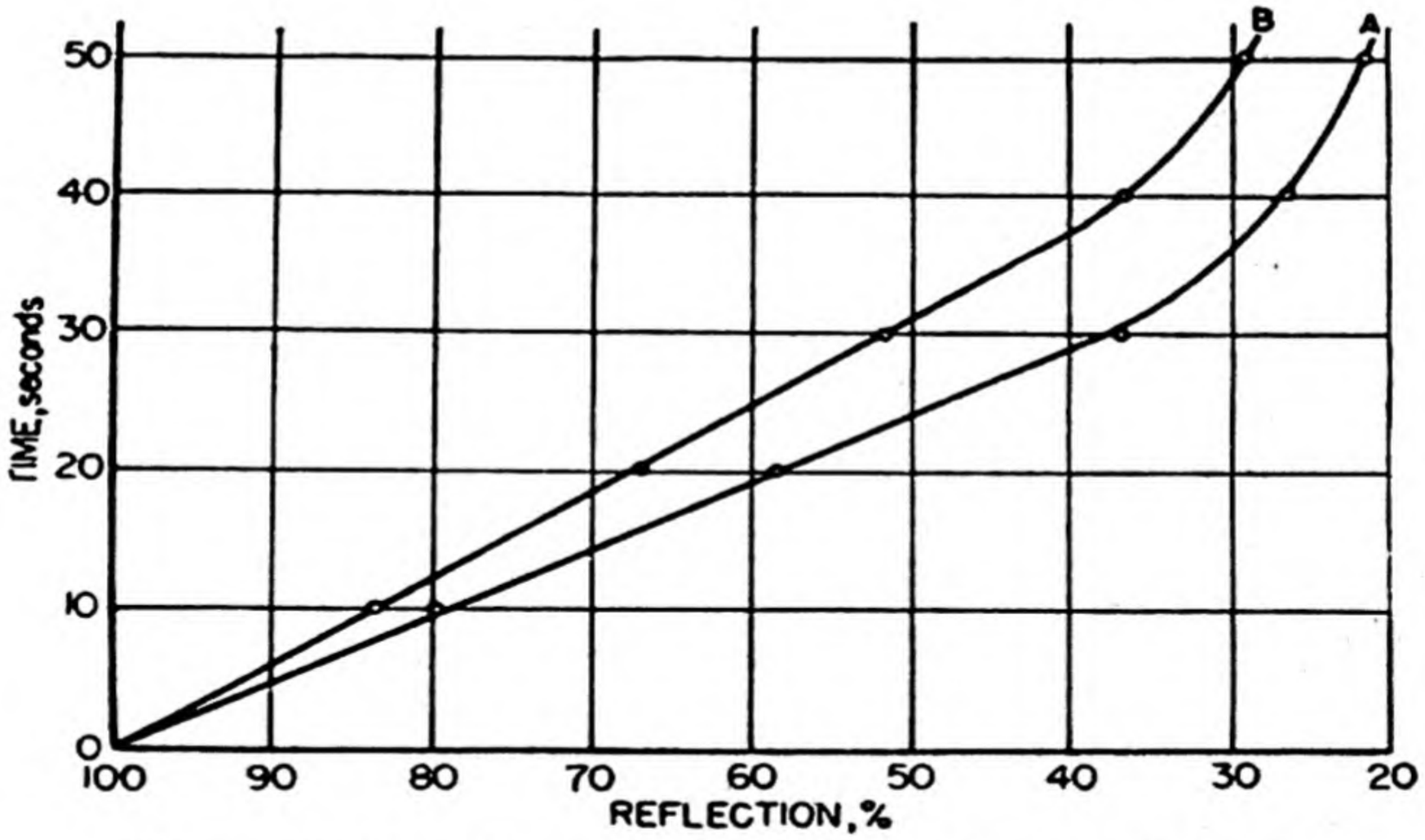


Figure XI-2. Reflection-time curve for two inks.[10]

penetration is, therefore, found as the slope of the linear part of the curve. This is indicated in Table XI–2 in which cotangent values

have been given to make the higher values correspond with the speedier penetration.

TABLE XI–2

Ink Penetration Speed on an Absorbent Paper

Ink	Penetration speed (cotangent)
Ink A	2.13
Ink B	1.61

In general this quite uniform penetration is found for many inks and papers, and the slopes of the reflection-time curves for each paper-ink combination accurately indicate the speed of penetration.

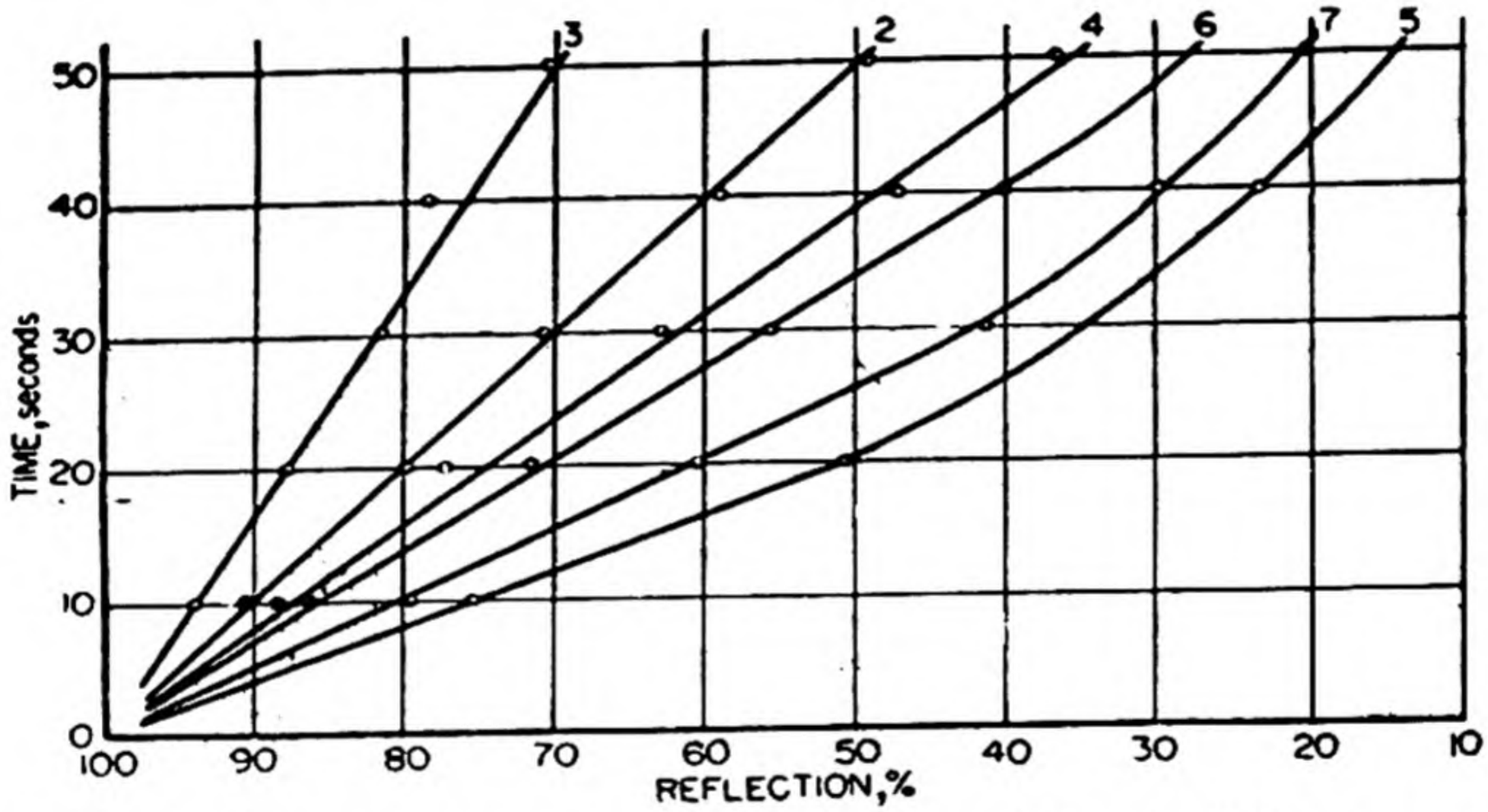


Figure XI-3. Reflection-time curve for a news ink on different papers.[10]

The influence of the paper is demonstrated in Figure XI–3 where the reflection-time curves are indicated for a number of different news stocks on which the same ink was allowed to penetrate. The results are also given in Table XI–3, showing the marked differences of newsprint of different manufacture.

The method is sensitive enough to show the difference between the penetration speeds of the two sides of a paper. Generally the ink penetration speed from the wire side is markedly higher than the penetration from the felt side.

The uniformity of commercial paper is usually poor, and even neighboring spots on the same paper sheet may show a considerable

difference in penetration speed for a standard ink. The use of a standard paper stock, for which Whatman filter paper No. 50 is recommended, yields much more constant results. More significant results are obtained by carrying out the tests at a given constant temperature and humidity.

TABLE XI–3

Penetration Speed of News Ink on News Stock

Paper	Penetration speed (cotangent)
2	0.99
3	0.63
4	1.27
5	2.50
6	1.47
7	1.96

The influence of the viscosity of the ink vehicle is given in Table XI–4, measured for inks containing 12 per cent of carbon black and allowed to penetrate in the same paper stock.

TABLE XI–4

Penetration Speed and Vehicle Viscosity

Vehicle viscosity, poises at 80°F.	Penetration speed (cotangent)
0.40	3.80
0.60	2.85
0.98	1.85
1.50	1.02
2.52	0.54
4.27	0.40

In Figure XI–4 the penetration speeds are plotted against the vehicle fluidities (reciprocal viscosities). A linear relationship is found. From these observations it may be concluded that the penetration speed of an ink is directly proportional to the fluidity of the ink vehicle and independent of the ink fluidity.

It was observed that homogeneous liquids made up by mixing components of different viscosities penetrate as a single liquid. This conclusion is not in disagreement with the separation of components

as a result of differences in adsorbability observed in paper chromatography. The thickness of the paper, of the order of 50–100 microns, is far too small to effect any detectable separation of ink vehicle components. In colloidal vehicles, however, mechanical separation of dispersed components is often found. Larger aggregates are filtered off and held mechanically in the superficial paper fibers. Sometimes separation occurs only in papers characterized by very fine pores, but not in paper with wider capillaries.

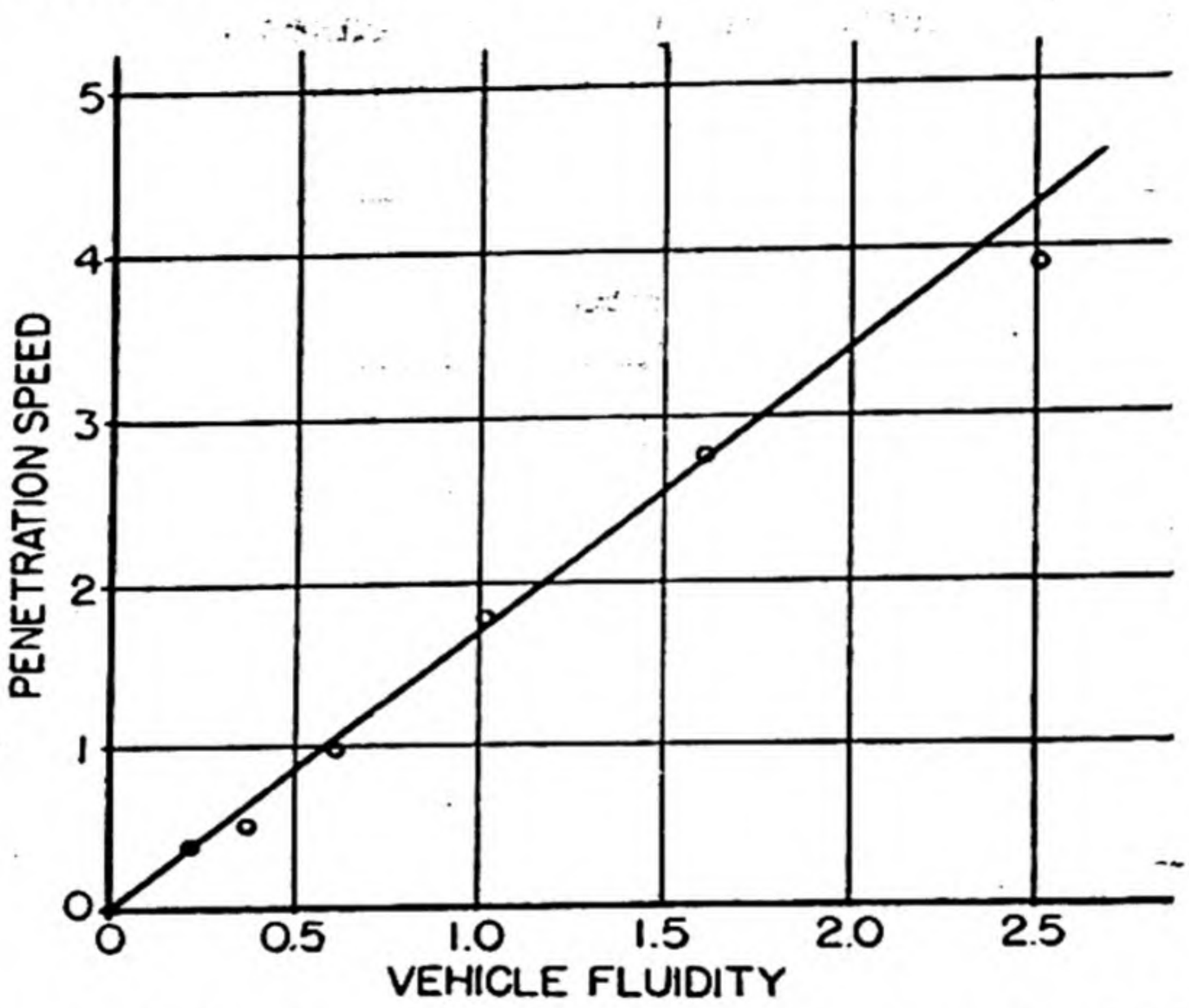


Figure XI-4. Relation between penetration speed and vehicle fluidity.[10]

Contrary to expectation no correlation between speed of vehicle penetration and surface tension of the vehicle was observed, more likely as a result of the very complicated changes which occur in the system when the vehicle penetrates, leaving the pigment behind.

The influence of the pigment concentration upon the speed of penetration was studied in other experiments. A series of inks were made using a mineral oil vehicle and pigments in varying concentrations, the penetration speeds of which were determined. Figure XI–5 shows the result for carbon black and lithol red. It is observed that for both pigments the penetration speed decreases rapidly upon pigment incorporation until a pigment concentration of about 6 per cent has been reached, after which the penetration speed shows only a slight decrease (lithol red) or remains practically unchanged (carbon

black), notwithstanding the fact that the dispersions examined varied from extremely fluid to viscous plastics. Similar results were obtained with the other pigments and with different vehicles, revealing a variation only in the concentration at which the constant penetration level was reached.

From these tests it appears that the use of a vehicle instead of an ink in penetration speed tests is not justified, in view of the large differences between the actual penetration speeds of inks and vehicles.

The speed of penetration of inks increases rapidly with increased temperatures. It was found that this change was due entirely to the

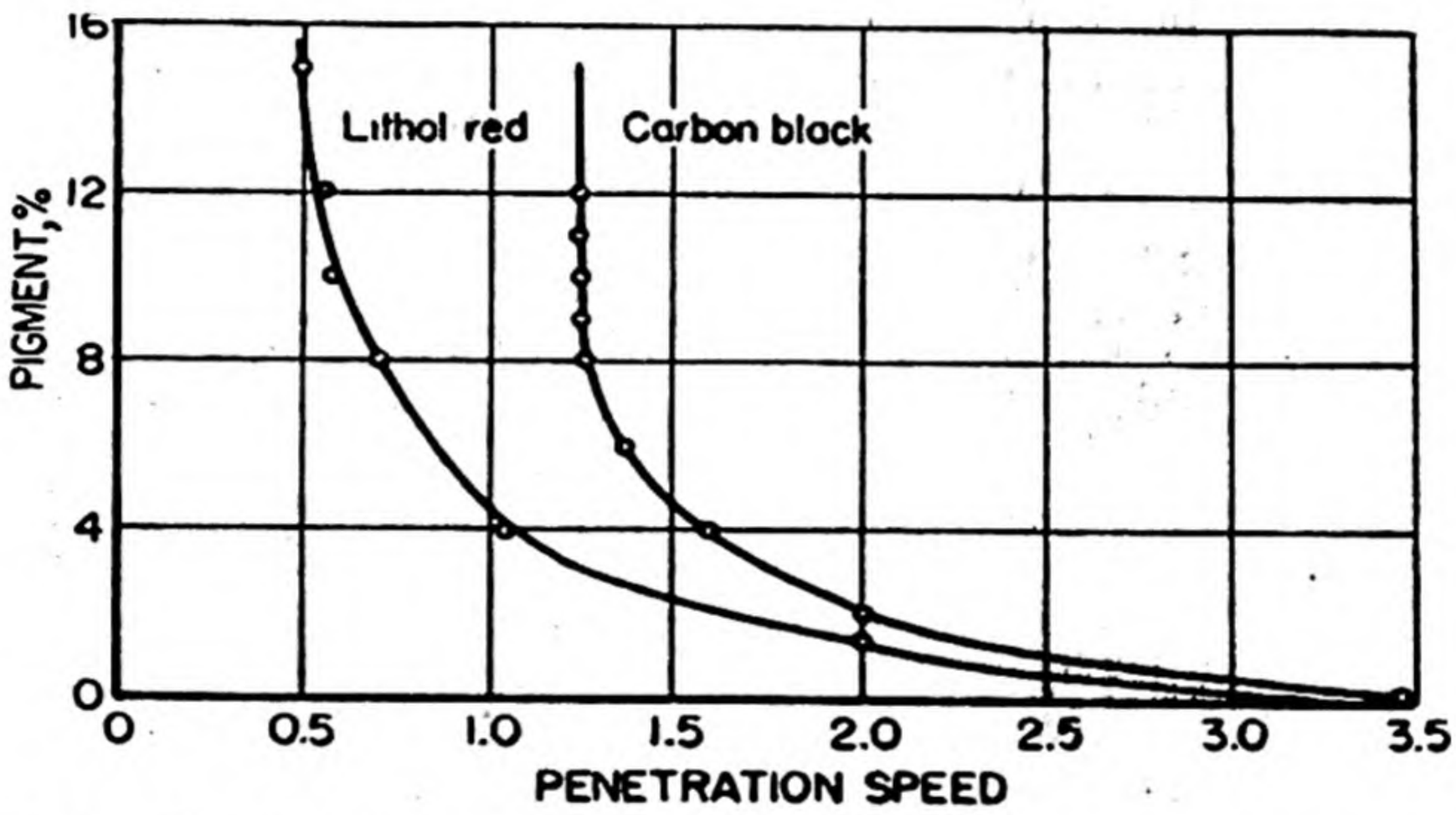


Figure XI-5. Relation between penetration speed and pigment concentration.[10]

change in vehicle viscosity. If the penetration speed is plotted against the vehicle fluidity at each temperature a linear relation is obtained, which is in agreement with the theory.

It must be acknowledged that the initial penetration of inks as a result of the printing pressure, a most important phase of the penetration of inks into paper, has not been considered in the described experimental procedures. The measurement of the initial penetration phase, lasting only a small fraction of a second, is beset with so many technical difficulties that a successful solution of the problem has not yet been published.

The described tests deal with penetration in depth in the paper. In view of the homogeneity of uncoated papers, the results are fully applicable to penetration of the surface layers of the paper.

In a study of the spreading of a drop of ink on a paper surface by means of a cylinder rolling down an inclined plate, Beckman[11] showed that the penetrability of the paper influences the area of spreading of the drop. There are, however, so many other factors involved, such as roller weight and speed, roughness of the surface, and rheological characteristics of the ink, that the method is too involved for a direct quantitative evaluation of the rate of ink penetration. Moreover, the predominantly tangential flow of the ink in this "nib spreading" procedure, utterly unlike the flow in depth as a result of the printing impression, makes this method fundamentally different from actual printing.

D. PENETRATION OF INK IN COATED STOCK

The methods described for the determination of the speed of penetration of ink into paper are not valid for coated stocks because actual penetration occurs rapidly in the coating and much more slowly in the body stock. The penetration speed through the stock, therefore, is basically the penetration speed through the body stock, immaterial for the setting of ink. It is therefore essential to measure the speed of penetration into the coating.

A method of measuring the surface penetration of an oil into a paper coating was developed by Vallandigham,[12] who determined the change in gloss with time of a paper surface on which an oil film had been deposited by a roller. The more rapidly the oil penetrated into the page, the more pronounced were the changes in surface gloss with time. The method is not easily adapted for practical paper evaluation, and the results cannot be expressed in a single numerical evaluation factor. Moreover, the oil penetration cannot be considered equivalent to ink penetration.

The so-called K & N test[13] has found wide acceptance as a quick evaluation of the rate of ink penetration on coated stock. It is essentially a smear test, using a nondrying ink with a soluble dye. The ink is applied on the coated stock, left for a period of two minutes, and then is removed. The color intensity of the remaining stain is compared with the stain intensity made under identical conditions on

[11] N. J. Beckman *et al.*, *Am. Newspaper Publishers Assoc. Research Bull.* No. 26, June 30, 1950.
[12] V. V. Vallandigham, *Pulp & Paper Mag. Can.*, 921, November 1945.
[13] *Research Bull.* No. 8, Lith. Tech. Foundation, New York.

a standard paper. A quantitative estimation of the stain intensity by means of a photoelectric densitometer, as advocated by Cahn,[14] allows a numerical evaluation of the penetration speed of the ink.

Voet and Brand measured the progressive intensification of the stain after prolonged exposure of the coated stock. Plotting the surface brightness against the elapsed time, both on a logarithmic scale, a linear function is obtained. This is shown in Figure XI–6 for different coated stocks treated with the same testing ink.

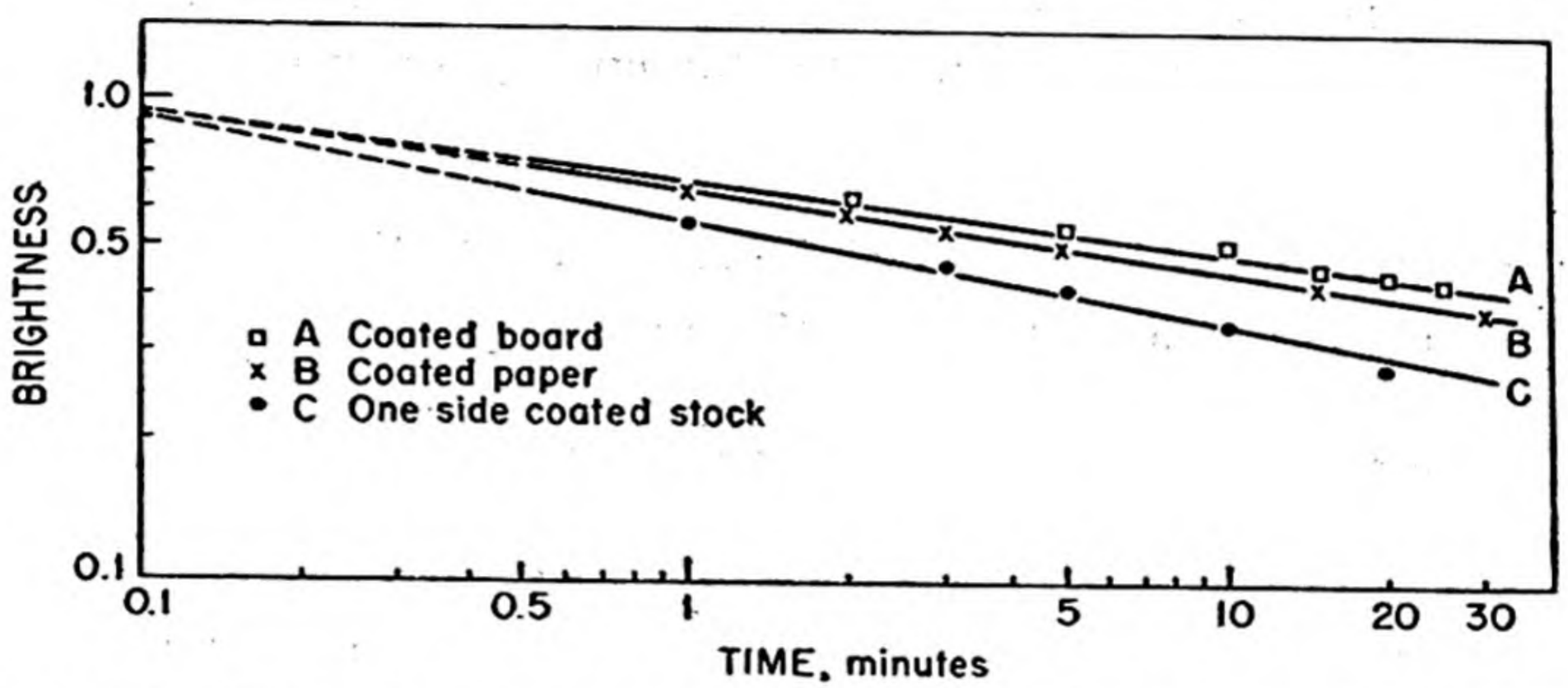


Figure XI-6. Change of surface brightness with time in stained coated stock.

From the linear relationship obtained, the following equation may be derived:

$$B_t = B_o t^{-k} \tag{38}$$

where B_o is the original paper brightness, B_t the brightness after the time t, and k a constant characteristic of the paper and indicated by the slope of the line. From the equation it is apparent that for a given test ink the constant k fully determines the rate of penetration of the ink into the surface of the coated stock.

The receptivity of a coated paper for printing inks, as indicated by the constant k, appears to be in agreement with paper evaluation determined by direct printing.

E. THEORY OF INK PENETRATION INTO PAPER

A very interesting though perhaps rather academic approach to the problem of ink penetration was made by Boyd-Campbell.[15] This

[14] L. Cahn, *Am. Ink Maker, 28* (5), 41 (1950).
[15] W. Boyd-Campbell, Pulp & Paper Institute of Canada, Report 56, 1945.

author considered the physics of flow of liquids through a capillary system. The flow of a liquid through a single capillary, originally derived by Poiseuille, is not valid for a system of interlocked capillaries. Kozeny[16] derived an equation for the flow of liquids through porous masses, taking into account that the passages are interconnecting and not of uniform cross section, which was applied by Boyd-Campbell. In addition, liquid flow follows a path through the system which is not necessarily a straight line. After introducing the concept of hydraulic radius, denoting the ratio of the total area of capillary passage cross section and perimeter, a relation is developed between paper permeability K, void fraction E, and hydraulic radius m as follows:

$$K = {}^1/_6\, Em^2 \tag{39}$$

The paper permeability may be determined by means of the Gurley densometer, taking into account an air viscosity of 1.82×10^{-4} poise. The void fraction of the paper is measured from the bulk of the paper and the density of its solid constituents or by saturation of the paper with a liquid which does not cause swelling of the capillaries. For an average newsprint a void fraction of 0.60 was found, indicating that the pores of the paper cover more than half the paper volume. From these data it was calculated that the average capillary radius in a representative newsprint is 0.26 micron. The total capillary surface area was calculated at about 150 cm.^{2} per cm.^{3} of paper.

Boyd-Campbell then proceeded to calculate the amount of ink pressed into the paper pores during the contact period in newspaper printing. Taking a pressure of 267 p.s.i., an ink viscosity of 40 poises, and a contact time of 0.002 second, it appears that all the ink should be pressed into the paper pores during the impression. Taking into account, however, the reduction in pore volume as a result of the printing pressure, it was estimated that somewhat less than half of the ink would penetrate. An estimation of the time necessary for the setting of the remainder of the ink was attempted by Boyd-Campbell, but the difficulties encountered were too great to make the quantitative result of much value. Yet, the approach he initiated of studying ink-paper interaction on a pure physical-chemical basis is extremely enlightening and promises a better fundamental under-

[16] J. Kozeny, *Sitzber. Akad. Wiss. Wien, Abt. IIa, 136,* 271 (1927).

standing of the basic phenomena connected with ink and paper interaction.

Tollenaar,[17] extending Boyd-Campbell's views, emphasized the distribution of pore sizes of the capillaries. For a good ink penetration it is stated that the large capillaries act in rapid absorption, while the small capillaries are required for an extensive diffusion of the ink. Such a desirable paper condition is obtained with a very flat distribution curve of the capillary dimensions or with a curve with more than a single maximum. A paper of long fibrous materials with small particles embedded provides a system which has the properties considered desirable.

[17] D. Tollenaar, *Chem. Weekblad, 44,* 753 (1948).

CHAPTER XII

PRINT-THROUGH

A. SHOW-THROUGH AND STRIKE-THROUGH

Print-through is defined as the phenomenon which causes a decrease of the surface brightness of the reverse side of a printed sheet. If a stained or colored oil penetrates through the paper, "strike-through" is said to occur. If the print is merely visible as a result of paper transparency, "show-through" is observed.

Strike-through is usually restricted to inks drying by penetration. It is seen where dark oils are used or where excess of soluble toners cause a diffusion of the soluble dye to the reverse side of the print. Strike-through is very undesirable, since it interferes markedly with the legibility of the text and the clarity of the halftones.

Crude dark ink oils have been used to promote flow in inks. The refining and decoloration of dark oils causes a decrease in flow qualities of the inks, which must be compensated by the use of surface-active resinous materials. Since these chemicals either are not colored or are so effective that they need be used only in small quantities, the vehicle color is not markedly affected. In addition, the use of the proper pigment often makes it possible to reduce the amount of resinous surface-active ingredients needed to provide flow in inks. For example, with carbon blacks in mineral oils, the use of pelletized black dispersed in a mineral oil by means of a ball mill at elevated temperatures eliminates much of the need for a resinous surface-active agent in the ink.[1]

Soluble dyes are often used in lower grades of black inks to correct the brownish hue inherent in channel black, in which the use of more expensive blue or violet pigments is not economically feasible. In recent times the less brown and more bluish furnace blacks have become available to the ink maker. The color strength of these blacks generally is only slightly inferior to the channel black strength. The use of furnace blacks in inks makes a color correction with soluble

[1] A. Voet, U. S. Patent 2,453,557, Nov. 9, 1948.

dyes unnecessary. Strike-through, therefore, is rarely seen in modern American newspaper printing. Show-through, on the other hand, is very familiar to newspaper readers. It is caused by paper transparency, which makes the print visible from the reverse side.

The unprinted paper may be fairly opaque, but when printed it may become transparent. This is caused by oil penetration, for in penetrating into the interspaces between the fibers the mineral oil used in news ink replaces the air. Since the refractive indices of oil and paper fibers are nearly identical, the paper acquires transparency at the printed spots, causing show-through. Although show-through caused by lack of paper opacity is independent of the type of ink used, it has been observed that this undesirable phenomenon, induced or increased by vehicle penetration, is restricted to inks drying by absorption which have a mineral oil basis. The lack of vehicle diffusion in inks with volatile solvents and the higher refractive index of drying oils minimize the effect in all but the conventional news inks.

In newspaper printing it is not often easy to differentiate between print-through and offset. Offset, caused by actual ink transfer on the paper surface, may be partly or completely erased with a rubber eraser, but print-through is not removable because show-through is on the reverse side and strike-through is throughout the entire paper depth.

B. MEASUREMENT OF PRINT-THROUGH

Strike-through and show-through cannot be evaluated separately. Both are interdependent, since they are caused or influenced by oil penetration into the paper stock. Bekk[2] combined measurements of color densities of prints with the determination of the maximum decrease in brightness obtained on the reverse side of the print. Figure XII–1 is a typical curve indicating the relationship of maximum print-through to blackness of print and film weight. It is observed that the print-through increases with increased blackness and film weight.

Mill and Colquhoun[3] studied the time dependency of print-through. A typical curve is shown in Figure XII–2. Initially a

[2] J. Bekk, *What the Printing Process Demands of Paper,* London School of Printing, London, 1935.

[3] C. C. Mill and J. W. Colquhoun, *Patra J.,* 215 (1940); *Am. Ink Maker, 20* (3), 20 (1942).

very rapid increase is noticed, accomplished in less than one minute. This is followed by a region of gradually decreasing rate of print-through. Finally a saturation value is reached. It appears that the initial decrease in brightness is not only extremely rapid, but the bulk of the entire effect takes place in the initial phase. Therefore,

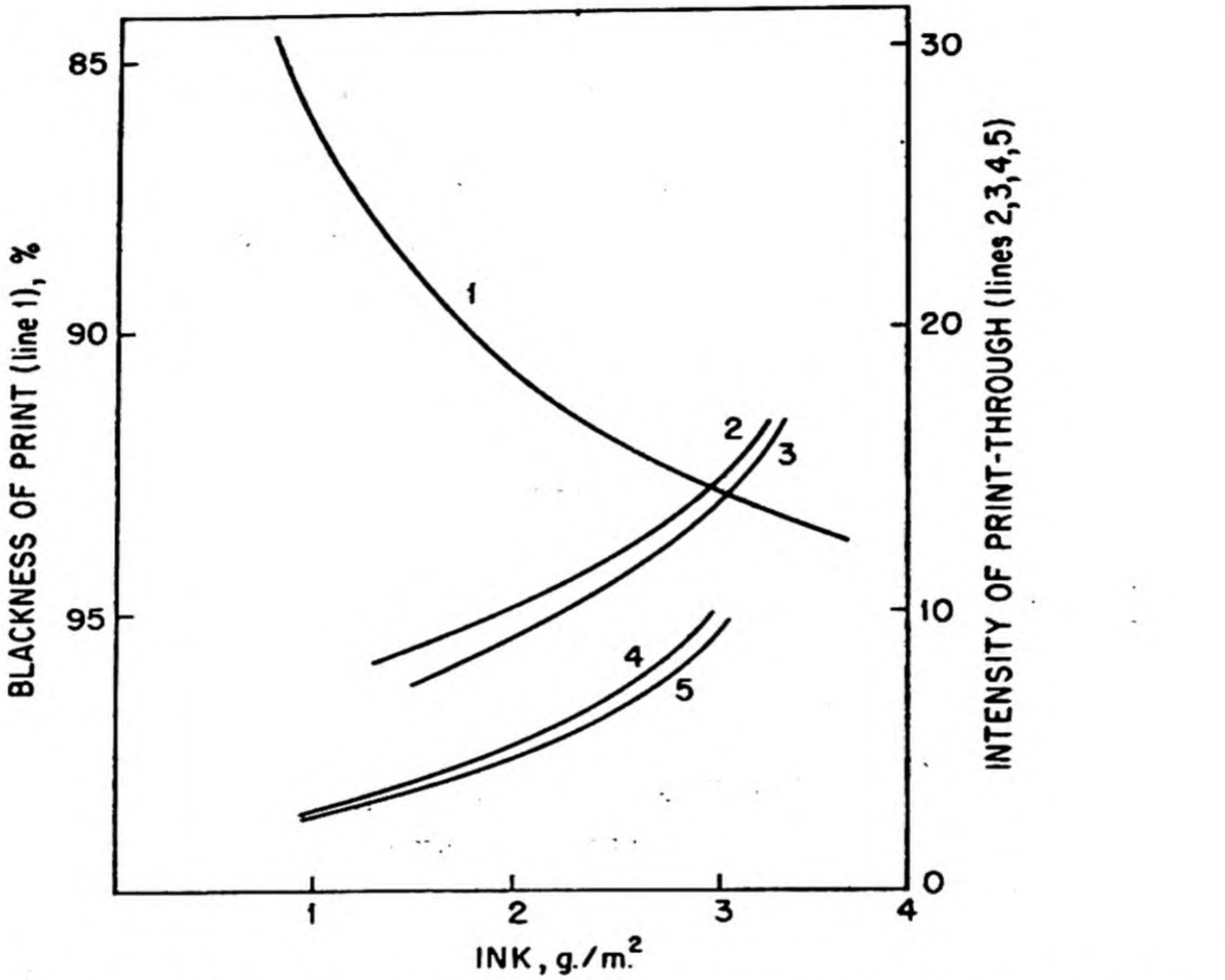


Figure XII-1. Relationship between print-through, blackness, and film weight: (1) blackness curve on paper a and b; (2) print-through on paper a after 48 hours; (3) print-through on paper a after 3 hours; (4) print-through on paper b after 48 hours; (5) print-through on paper b after 3 hours.[2]

for all practical purposes print-through occurs in the first ten minutes after printing. For most inks on news stock a final value is generally reached in two hours. For thinner films the end point is reached in a shorter period of time.

According to Mill and Colquhoun a linear relationship exists between the print-through P and the film thickness (film weight) W of the form

$$P = KW + L \tag{40}$$

where K and L are constants. K represents the tendency to cause print-through in the particular paper-ink combination, while L represents the decrease in brightness of the reverse side of the paper in the absence of oil penetration. The approximate character of this relationship becomes apparent from a closer examination of available data.

The mechanism of show-through was studied by Voet and Brand[4] in their investigation of the speed of penetration of inks in paper, discussed previously. A linear decrease in surface brightness was found in the initial phase of the ink penetration, so that the slope of the line indicating the decrease of brightness with time is identical

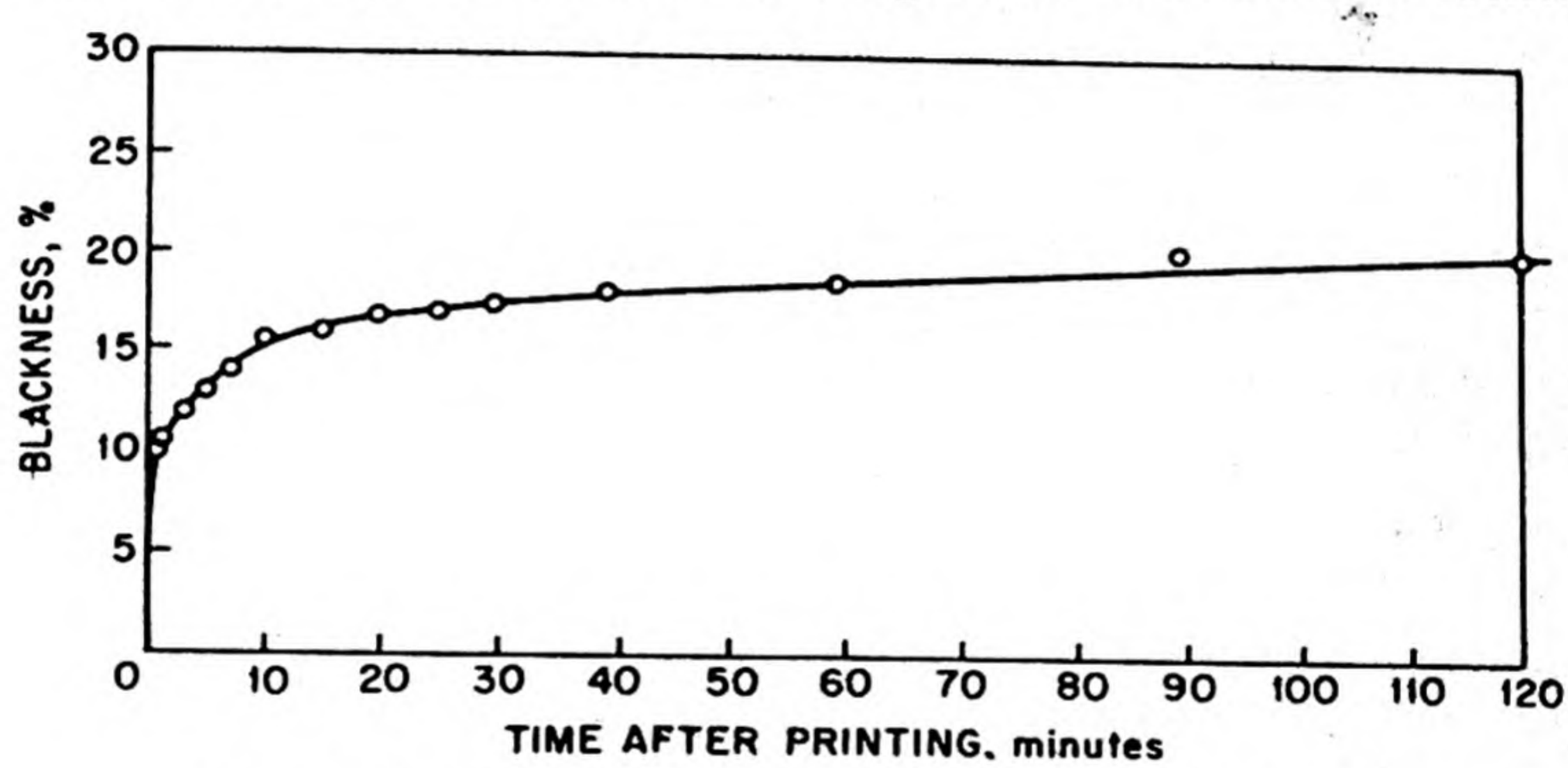


Figure XII-2. Increase of print-through with time.[3]

with the constant K of Mill and Colquhoun, and the penetration speed, therefore, is the reciprocal value of the constant K. For many papers, though not for all, Voet and Brand found that the penetration speed curves passed through the origin, indicating a value $L = 0$.

Mill and Colquhoun tested the print-through for various papers with a given standard ink. Assuming the validity of Poiseuille's law for oil penetration, which is an approximation only, the depth of penetration of an oil into paper was derived as

$$d = a\sqrt{St/\pi} \qquad (41)$$

in which t is the time of penetration, S the surface tension, and a a constant involving the mean pore size of the paper and the interfacial tension between oil and paper. The constants K and L, as related to

[4] A. Voet and J. S. Brand, *Paper Trade J.*, *122* (24), 35 (1946).

a and to the paper opacity p (expressed as contrast ratio) are indicated in Table XII–1.

A general tendency may be noticed for print-through to decrease with increase in oil penetration time. The influence of the ink composition on the print-through is very marked. It was found that the

TABLE XII–1

Print-Through and Paper Properties[3]

Paper	a	K	P	L
1	0.43	2.9	0.943	0
2	0.45	3.2	0.925	0
3	0.50	2.7	0.925	0
4	0.57	2.9	0.915	0.7
5	0.38	2.4	0.945	0
6	0.66	4.6	0.860	2.5

less viscous the ink vehicle, the more pronounced the print-through. The influence of the pigment concentration is more complex. A decrease is observed between 5 and 20 per cent of carbon black and an increase between 20 and 30 per cent. Table XII–2 summarizes the

TABLE XII–2

Print-Through and Ink Properties[3]

Pigment, per cent	Print-through in per cent, for vehicle viscosities (in poises at 20°C.)		
	2.5	37	62
5	13	7	9
10	5.5	3	3
15	4	3	3
20	4.5	2	2
25	5	2.5	2
30	8	2.5	—

dependency of the maximum print-through on ink composition for inks made by dispersing a carbon black in mineral oil vehicles of different viscosities.

From Table XII–2 it is apparent that for both ink and paper a better adaption to high-speed printing requirements, such as a more

open paper structure and a faster penetrating ink, will lead to an increased print-through. Only a basic change in conventional news ink composition and in paper manufacture could overcome this unsatisfactory condition which is materially affecting present day newspaper printing. Both heatset and steamset processes provide for instantaneous ink setting, resulting in the reduction of print-through to its minimum value determined by the transparency of the stock.

CHAPTER XIII

INK TRANSFER

A. FACTORS INFLUENCING TRANSFER

A basic step in the printing process is the transfer of ink from form to paper, accomplished through splitting of the ink film.

Occasionally ink is not transferred at all, such as with a dampened ink-repellent lithographic plate or a mercury-treated copper plate, which do not accept ink. In such cases the ink does not wet the plate and no transfer can take place. If the ink film wets the surface, however, there is always ink transfer.

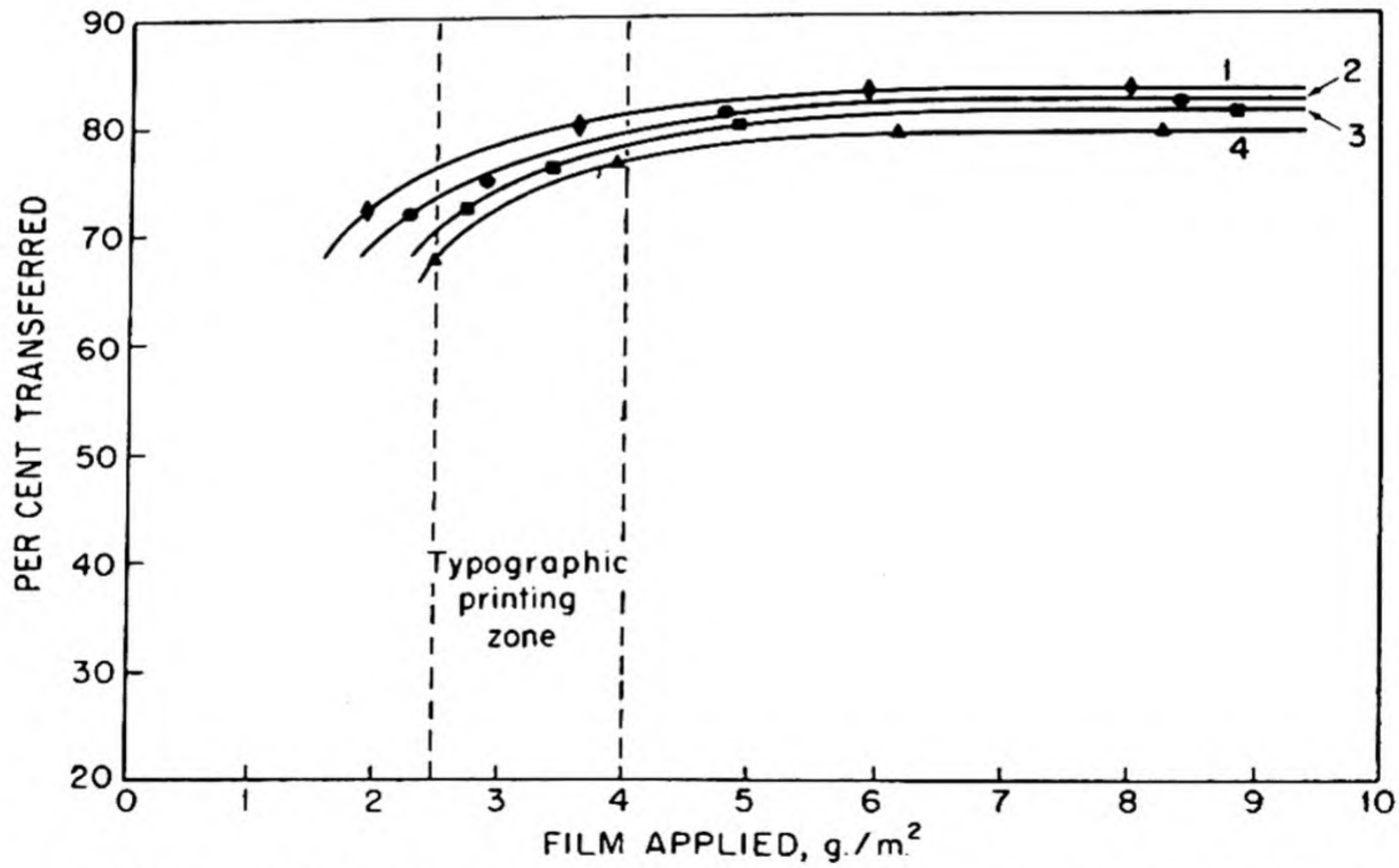


Figure XIII-1. Ink transference for different inks of varying film weights.

Ink transfer is conveniently measured by a simple gravimetrically controlled method of printing on a proof press, in which the amount of ink transferred is determined by the difference in weight of an inked plate before and after printing. Figure XIII–1 shows transference values plotted against film weights for four different black news inks on news stock at room temperature, using a Van der Cook

No. 4 proofing press. Table XIII–1 shows the physical characteristics of the inks used.

It thus appears that notwithstanding the great variation in ink characteristics, ranging from low to high viscosity and from low to high speed of penetration, the various curves obtained do not show a great deal of difference. All are characterized by an initially rapid and later a more gradual increase of the percentage of ink transferred, as an increased quantity of ink is applied, until a maximum is reached when about 80 per cent of the film is transferred to the paper.

TABLE XIII–1

Ink Characteristics

Ink	Viscosity, poises at 80°F.	Penetration speed (cotangent)
1	33	0.27
2	8.6	0.27
3	24	0.95
4	160	0.04

Figure XIII–2 shows the transference values for a news ink on news stock, coated stock, glassine, and cellophane. The general shape of the curves is the same as that of the curves in Figure XIII–1, but the maximum differs, being at 50 per cent transfer for cellophane, 48 per cent for glassine, and 70 per cent for coated stock. The data given show conclusively that the smoother the stock, the less the ink transfer. The influence of ink absorption is not pronounced, although the more rapidly penetrating inks show a larger percentage transferred.

Figure XIII–3 shows the results for ink transfer measurements from metal to rubber and from rubber to paper for a litho ink made by incorporating 30 parts of carbon black into 70 parts of bodied linseed oil. The transfer to the rubber blanket is 50 per cent, while from rubber to paper it is 76 per cent, resulting in a total transference of 38 per cent, characteristic for offset lithography. The low pigmentation required in newspaper printing, the medium pigmentation used in magazine typography, and the extremely high pigment loading essential in offset lithography are explained by the differences in ink transfer under the conditions prevailing in each process.

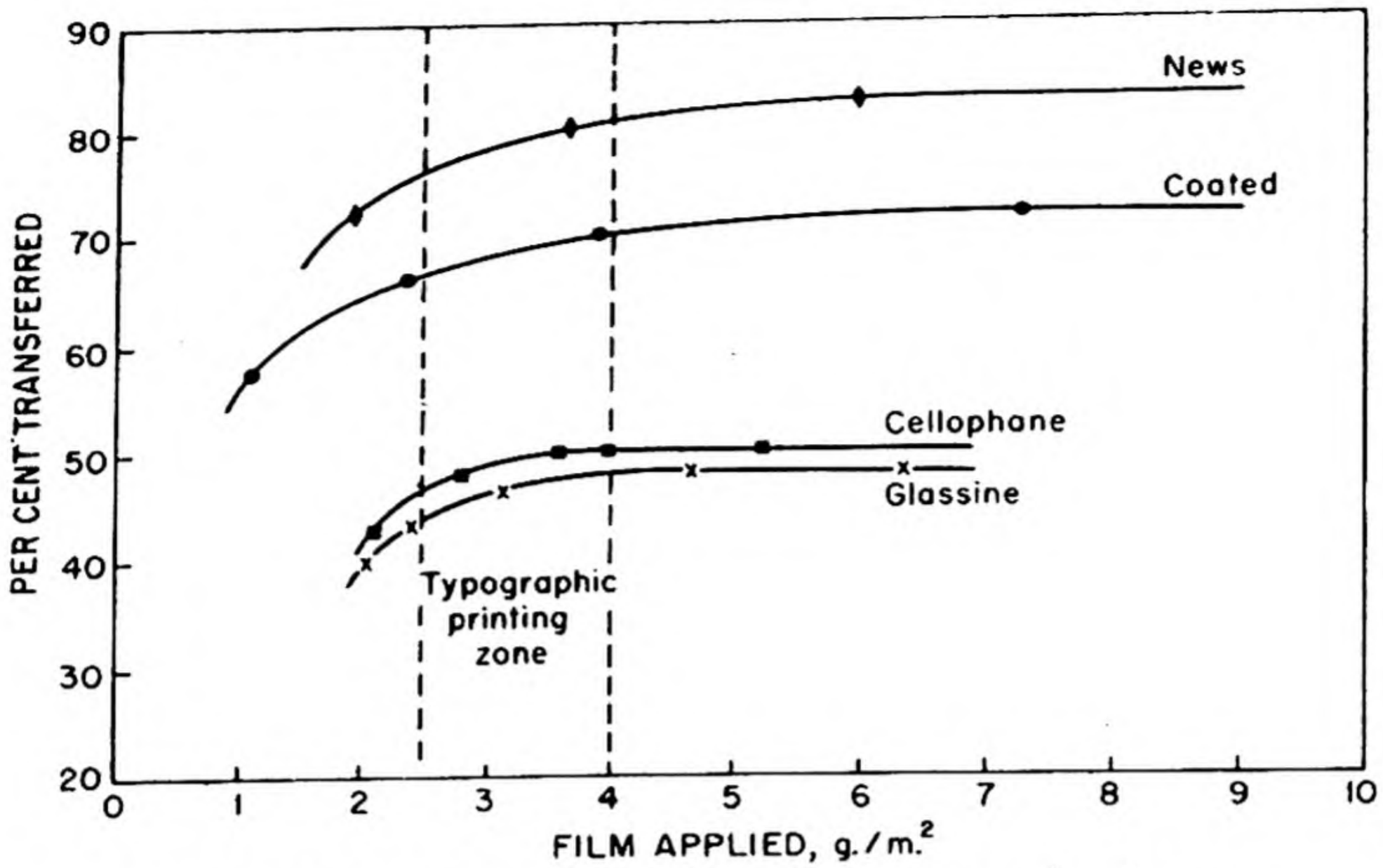


Figure XIII-2. Ink transference on different surfaces.

In a series of experiments on ink transfer, Mill and Colquhoun[1] found that all polished metal surfaces show the same percentage of ink

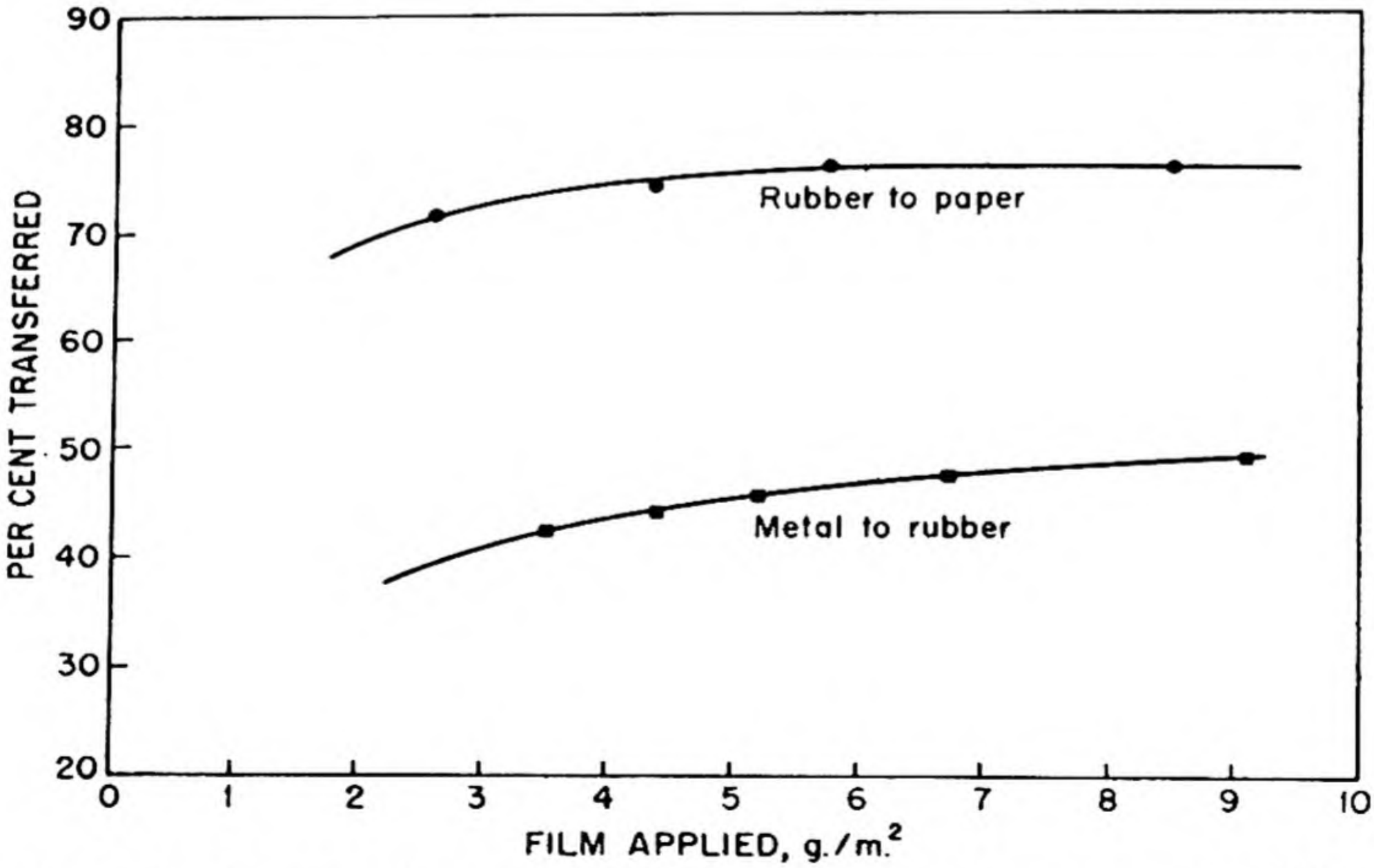


Figure XIII-3. Ink transference metal-rubber and rubber-paper for litho inks.

[1] C. C. Mill and J. W. Colquhoun, *Patra J.*, 215 (1940); *Am. Ink Maker*, *20* (3), 29 (1942).

transferred, regardless of the metal. By roughening the surface, however, it was noted that the percentage transferred decreased as the surface roughness increased.

The effect of pressure on ink transference may be investigated by packing up the plate. It was found that the percentage of ink transferred increased regularly with the thickness of the packing. Poulter and Croney[2] found increased ink transfer at increased pressures, with a gradually diminishing increase until a saturation value is reached at about 700 p.s.i. The importance of these observations for the understanding of the process of make-ready is obvious. Make-ready by regulating the height of the form actually determines the printing pressure and thus the percentage of ink transfer at each spot. The entire process of make-ready, therefore, depends upon the change of the ink transference with the printing pressure.

The influence of temperature and humidity upon ink transfer was investigated under normal conditions of variations existing in the pressroom, involving a change of humidity of 40–90 per cent and a change of temperature of 70–90°F. The variations were only slight, and the main character of the curves remained entirely unchanged.

Mill and Colquhoun[1] indicated the existence of a decrease of the transference percentage for a very large film thickness and for inks with a high pigment percentage. They claimed that a partial separation of oil and pigment occurred and stated that this abnormal transfer is the cause of the decrease in the percentage of film transference. A careful analysis of the original, transferred, and remaining film, however, by A. Voet showed that no abnormal transfer actually occurs, since the composition of the ink films were found to be identical. It was shown by Pihl[3] that the maximum in the ink transfer curve which is followed by a slow decline at greater film thicknesses, actually exists for all absorptive papers under printing conditions, but is not found for smooth, nonabsorbent stocks.

The influence of the speed of film separation has been extensively discussed in Chapter III, where it was indicated that at low pressures and at low transference the percentage transferred is proportional to the contact time, or inversely proportional to the rate of film separa-

[2] A. C. Poulter and R. G. W. Croney, *World's Paper Trade Rev., 115,* TS 2 (1941).

[3] L. Pihl, *Grafiska Forskningslaboratoriet, Medd. Nr 28,* 44 (1952).

tion. At higher values of transfer, however, a saturation point is rapidly reached.

Pihl and Olsson[4] investigated extensively the transfer of viscous oils and inks on a press under actual printing conditions. They generally confirmed the influence of pressure, printing speed, and film thickness as indicated above.

B. MECHANISM OF INK TRANSFER

In an investigation of ink transfer, Beckman and coworkers[5] showed that the mechanism of transfer may be understood by considering the differences in smoothness and absorptive qualities of the paper. They observed, upon shearing an ink film between two smooth nonabsorbing surfaces, that the division is generally equal, the transfer being thus 50 per cent. If one of the surfaces is rough, while the other is smooth, a certain quantity of ink adheres to the rough surface, while the remainder is split about evenly. As a result the ink transfer to the rougher surface is larger than 50 per cent. With roughened metallic surfaces, however, the differences are not marked and the transfer never exceeds 54 per cent.

If one of the surfaces is porous, ink will penetrate into the pores and again, the remainder will split evenly. This will result in a greater transfer of ink to the more absorptive stock, causing a transfer larger than 50 per cent. For thin films and absorptive surfaces the quantity of ink penetrated is significant and transfer may materially exceed 50 per cent. A large increase in ink transfer is seen in stocks which are both rough and absorptive.

The influence of absorbed and adhering ink, however, is limited and a saturation value is rapidly reached. At very large film thicknesses, therefore, the transfer values should again approach 50 per cent, regardless of their initial, high values, in view of the relative insignificance of absorbed and adhering quantities of ink compared with the total amount available.

Upon investigating very heavy films by means of a rolling cylinder, of thicknesses up to 50 microns, far beyond the printing range, Beckman[5] actually observed the gradual decline of the transferred percentage of ink and the asymptotic approach to the 50 per cent value.

[4] L. Pihl and I. Olsson, *ibid., Nr 28,* 58 (1952).
[5] N. J. Beckman *et al., Am. Newspaper Publishers Assoc. Tech. Report* No. 5, May 5, 1952.

Thus, ink transfer curves extended to such large film thicknesses all show an initial flat maximum and a slow decline, as is indicated in Figure XIII–4.

The higher the printing speed, the less is the penetration, in view of the reduced time of contact. Consequently at higher speeds ink transfer values will approach the 50 per cent mark at a smaller film thickness than at slower speeds. It thus appears that the area under the transfer curve above the 50 per cent line is a measure of ink absorption for absorptive smooth stocks and of absorption superimposed on adherence for absorptive rough stocks.

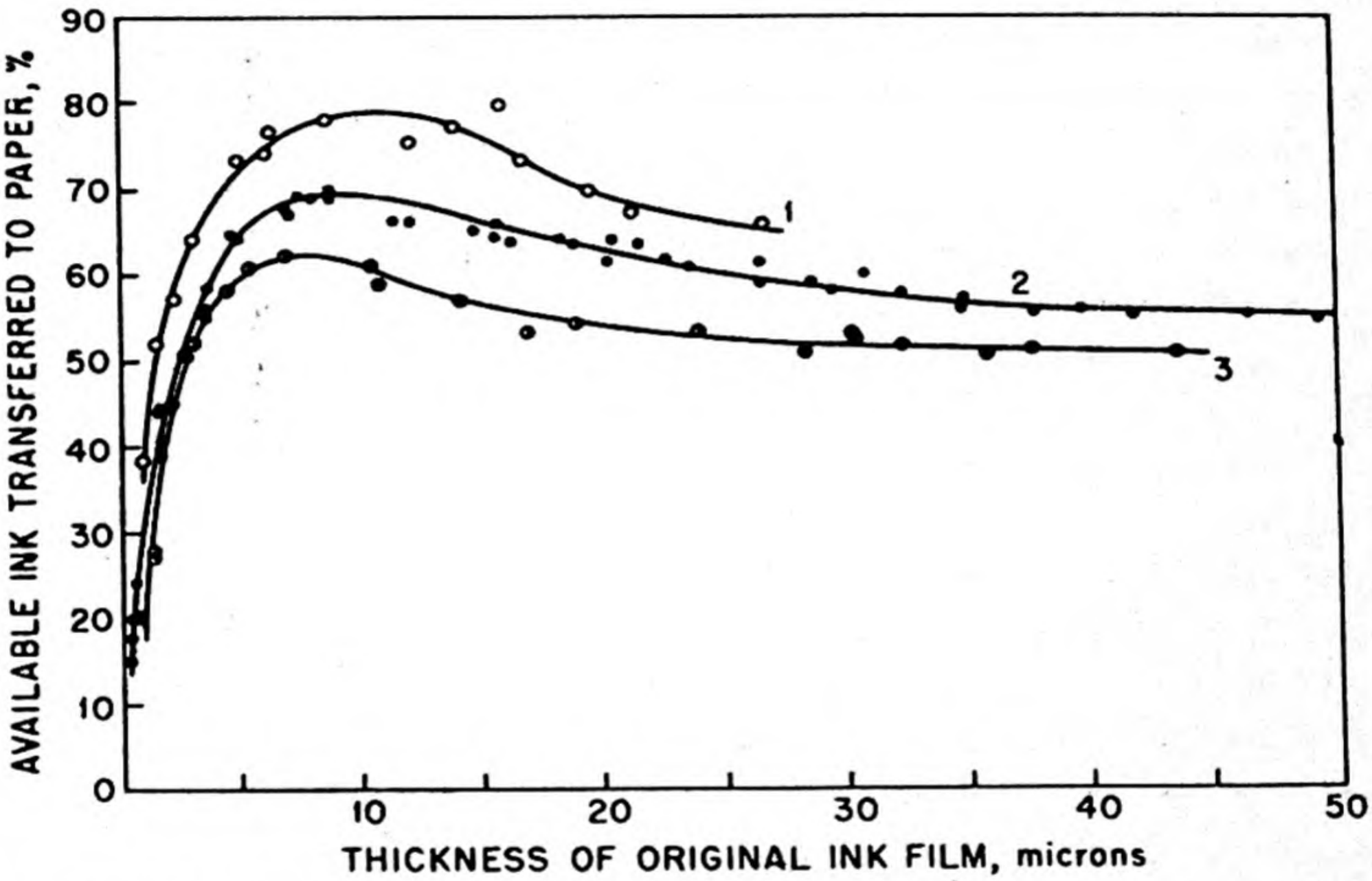


Figure XIII-4. Ink transfer curves extended to large film thicknesses.[5] Roll speed: (1) 20 cm./sec.; (2) 80 cm./sec.; (3) 160 cm./sec.

The percentage of ink transferred for ink films of very small thicknesses is low. It appears, however, that with very thin films contact is incomplete and the contact area is much smaller than the actual area. As a result, ink transfer is reduced and reaches its maximum value only at larger film thicknesses, after complete contact has been established.

It must be emphasized that an even split of an ink film sheared between identical surfaces is only reached at the relatively high printing pressures of about 700 p.s.i. prevailing on commercial presses.

At much lower pressures, such as are obtained with the rolling cylinder tackmeter previously described, transfer is generally well below 10 per cent, even with exceedingly heavy films of thicknesses up to 80 microns. Upon increasing the pressure, the percentage of ink transferred increases until finally the limiting, saturating value has been reached, which amounts to exactly 50 per cent transfer between identical surfaces.

The increase in percentage of ink transferred between identical nonabsorbent surfaces with pressure makes it clear that forces extending from the surfaces cannot play any significant part in the process of film transfer. This is obvious, since molecular forces extending effectively over a distance of microns, many thousand times the diameter of the molecules involved, are unknown. The explanation of film transfer, therefore, must be of a different nature, based solely on phenomena occurring in the ink film.

As extensively discussed in Chapter III, the process of film separation at printing speeds is of an impact nature. At impact the rate of deformation of the ink film is very high and its propagation may even be in the nature of a shock wave.

It has been shown that the process of film separation is dominated by the maximum energy which the film is able to absorb before rupture. This quantity, denoted as tack energy, was measured accurately for a variety of inks and surfaces at different speeds. When rupture occurs, stress exists at the impact end, and the energy distribution in the wave is such that, due to a rapid damping of the vibration, the rest of the sample is unaffected. The transferred film is therefore the part which has absorbed the rupture energy. Since the film is an isotropic body (one which has the same physical properties in all directions), the exact location of the place of rupture will depend on the distribution of stress and strains in the film and is not affected by local weak spots.

It may be stated that at higher pressures, corresponding to higher amplitudes, the damping of the oscillation is accomplished at a greater distance from the place of impact than at lower pressures and lower amplitudes of vibration, leading to increased film transfer at increased pressure. The following is a possible explanation of film transfer.

There are indications that near the saturation point, corresponding to the maximum percentage of ink transfer, the effect of the damping of the oscillation is so reduced that the stress waves are

reflected and superimposed on the original wave front, resulting in a condition resembling a standing wave. Rupture will occur, in the absence of weak spots in the isotropic film, at the greatest amplitude corresponding to the highest energy density, which is in the exact center of the film for identical surfaces. Such a hypothesis might account for the unusual aspects of ink transfer, whereby a constant volume fraction of the film is transferred.

C. TRAPPING

Trapping is defined as the transfer of one film of ink on another in multicolor printing. Ink films which show a uniform transfer are said to trap properly.

In trapping, differences exist between wet and dry multicolor printing. In the dry process the ink is allowed to dry partly before the next ink film is printed.

From a series of tests it appeared that the adhesion of a printed ink film for other films increases rapidly after printing, goes through a maximum, and thereafter decreases markedly, corresponding to an increase, a maximum, and a decrease in surface tackiness of the drying film. The transfer of an ink film on a second, previously printed film depends on its degree of tackiness, and therefore on the drying stage of the drying film. As a result the second film will easily transfer to the first film during a certain period after the first ink has set. The transfer will be less satisfactory after the initial period and, finally, after the first ink has dried completely, ink transfer will be wholly unsatisfactory. The ink is said to have crystallized and no longer accepts the other ink. The failure of trapping in dry multicolor printing therefore is generally a failure of the proper timing of the second impression. It may be corrected by better timing or by an adjustment of the drying speed of the first ink.

In wet multicolor printing the second and succeeding inks follow the first ink much more closely and are often printed one after another, in quick succession, in the same operation. With this method there is no problem of adhesion of the wet ink films, but the condition may arise where the adhesion between successive ink films is stronger than the cohesion in the first film. In this case the first film is split and partly stripped from the paper. A requirement of proper trapping in wet printing is therefore the maintenance of a careful balance

between the cohesion and tack in the ink. For example, in four-color printing, the first color down, usually a yellow, is the tackiest, followed by a decrease in tackiness of the red, the blue, and the black, in the conventional order of printing.

A considerable complication is caused by the fact that at the moment of printing the inks are subjected to shear, resulting in rheological properties distinctly different from those at rest. For an exact prediction of the correct sequence of trapping it is essential to determine the tackiness of each ink at the actual speed of printing. The inkometer, discussed extensively in Chapter VI, is an instrument suitable for the determination of the proper sequence in wet multicolor printing at the desired speed.

From a study of inkometer data it appears that the tackiness of inks shows pronounced differences in their variation with speed, and a satisfactory sequence at one speed may be unsatisfactory at another. The fact that a sequence of tackiness at low rates of shear is occasionally completely reversed at high rates of shear is responsible for the failure of the conventional "finger-tap" method of tack evaluation in high-speed wet multicolor printing.

The vibrational theory of film separation is in accord with the general facts described above. In dry multicolor printing lack of adhesion, as a result of failure of proper wetting of a dry ink film by fresh ink, prevents proper ink transfer, regardless of the mechanism of transfer. In wet multicolor printing a shock wave is induced at the point of impact which is propagated in both films, the first as well as the second, the impact being on the interface. Consequently either film may rupture. The film which is able to absorb the most energy without rupture survives the impact wave, and film separation occurs in the film with the lowest tack energy density. In accordance with the observed facts, therefore, proper transfer occurs only when each successive film has a lower tack energy density than the one immediately preceding it.

CHAPTER XIV

PICKING OF PAPER

A. PICKING IN PRACTICAL PRINTING

In the printing process the separation of the paper-ink-plate union immediately after the impression occurs normally in the ink film. Under abnormal conditions it may take place in the paper. This phenomenon, characterized by partial or complete rupture of the paper stock, is known as "picking" or "plucking."

Picking may be observed as minute spots on the print, causing lack of uniformity and a decrease in the quality of the reproduction. In more pronounced cases of picking the entire surface may be torn apart, or the entire coating of a coated stock may be ripped off. Picking is always due to an ink which is too tacky for the particular conditions prevailing at the press.

One remedy for the undesirable manifestation of picking is to reduce the ink tack by modification or dilution of the ink or by raising the temperature in the pressroom. Another remedy is to reduce the printing speed, since the forces acting to disrupt the paper surface decrease in proportion to the reduction in rate of film separation. Finally, picking may be overcome by using a paper stock with a higher resistance to picking, or a coated stock in which the adhesive bond between coating and body stock is strengthened.

The actual information available on picking in a pressroom under controlled conditions is very meager. In a series of printing tests designed to study the phenomenon of picking, Bekk[1] investigated picking by printing different inks on different papers, by means of a Miehle vertical press at low, medium, and high speeds. The temperature and humidity in the pressroom were kept constant. A specially designed form was used which had solids and screens of three different sizes, each with highlights, middle tones, and dark tones. The solid pattern of the form ended in protruding shapes with vari-

[1] J. Bekk, *Druksnelheid, Drukinkt en Papier*, G. H. Bührmann, Amsterdam, 1937.

ous obtuse, right, and acute angles, where the printing pressure was expected to show sharp differences. The paper had been carefully conditioned to pressroom temperatures and humidities.

Picking was not found to occur at the borders of the solids, at the highest printing pressure, but more inwards. It was observed that at the maximum printing pressure, found near the specially designed pointed "tentacles" of the form, no picking at all took place. Picking was markedly less in the darker screens than in the solids. No differences between screen sizes were noticed in picking.

By increasing printing speed picking was gradually promoted. It was noticed, in a few cases, that upon increasing the speed picking very markedly increased initially, but dropped again. After about half a minute no further changes were observed and picking was stabilized at a somewhat higher level. This peculiar phenomenon, attributed by Bekk to a change in ink behavior at the higher press speed, was rather uncommon.

In comparing the various inks it appeared that the most viscous ink showed the most pronounced picking, although no measurements of ink viscosity at higher speeds were taken. The influence of the film thickness was not very clear. Bekk noticed that picking increased upon increased inking, but attributed the effect to increased sideways displacement of the excess ink, thus increasing the inked areas. In addition, it was noticed that small air bubbles were removed with excess inking, causing a more complete union between ink and paper. It was also found that quickly penetrating inks generally promote picking. Calendering of paper decreased resistance to picking as a result of the tension caused by the forceful mechanical displacement of superficial fibers. Smooth papers show more picking than rougher papers, while an open paper structure seems to be more subject to picking than a closed paper structure.

From these observations it appears that picking under actual printing conditions is a complicated phenomenon, strongly influenced by paper, ink, plate, press, and speed of printing.

B. TESTING OF RESISTANCE TO PICKING

Various methods have been developed to test empirically the resistance to picking of a paper. In the wax strength test a series of standard waxes, numbered in order of progressively increasing ad-

hesiveness, are applied in a melted condition to the paper surface. After solidification the wax is pulled off at right angles from the paper with a quick jerk. The number of the highest adhesive wax which the paper will stand without damage to its surface is reported as the critical wax strength number.[2, 3] It is not surprising that the correlation between this number and the actual resistance of a paper to picking is unsatisfactory.

A number of rotary pick testers have been developed which all roughly imitate the printing process. A viscous reference liquid is usually applied by an inking mechanism in a predetermined film thickness on a form roller. The latter is applied to the paper with a given pressure at increasing speeds. The lowest speed at which picking is observed is then accepted as a critical value for the resistance of the paper to picking.[4-6] While the data obtained are reproducible at constant temperatures and humidities, the correlation with actual printing is only fair. At best, empirical limits may be established for a satisfactory paper performance on a given press for a given speed only. A more fundamental approach appears to be possible.

C. ENERGY DENSITY OF RUPTURE

Picking is a manifestation of the process of separation of form and paper. Since the process is of an impact nature, the energy of rupture must be considered of primary importance.

The rolling cylinder tackmeter affords a rational determination of the resistance to picking of a given paper stock by measuring the energy density of rupture. A simple way to determine the energy of rupture is to increase the speed of the cylinder. As the speed approaches the rupturing point, an increasing number of small areas where parts of the paper are damaged are noticed. Such areas may indicate local weak spots in the paper and are generally discarded. As roller speed is further increased, and reaches a surprisingly sharply defined velocity V_r, the entire paper is ruptured. The corresponding energy density of rupture is then determined according to the method

[2] W. A. Kirkpatrick II, *Paper Trade J., 109* (12), 36 (1939).
[3] TAPPI Tentative Standard T 459 m-45 (1945).
[4] W. W. Roehr, *Proc. TAPPI, 34* (11), 575 (1951).
[5] J. F. Monroy, Symposium on Printing Inks, A. C. S., New York, 1951.
[6] Institute of Paper Chemistry, Report No. 31, parts I, II, III, 1941–1942.

described in Chapter III, the rupturing energy being equal to the tack energy density of the ink at the rupturing roller speed.

A large number of tests with different inks indicated beyond doubt that the rupturing energy density is independent of the film thickness of the ink under the conditions of the experiment. The fact that contradictory reports are found in the literature about the influence of ink film thickness in picking must be ascribed to the complications arising in actual printing, as discussed above. In addition, the conditions found in a pressroom are generally not carefully controlled.

Table XIV–1 shows the rupture energy density D_r for different papers, measured with the aid of different vehicles of Newtonian flow properties.

TABLE XIV–1

Rupturing Energy Density for Various Liquids on Different Stocks

Stock	Vehicle	Temp., °C.	Per cent relative humidity	V_r cm./sec.	D_r ergs/cm.
Coated A	Min. oil	27.5	69	228	3.23
	Varnish I	28.1	66	204	3.21
	Varnish I	27.1	66	165	3.23
News A	Min. oil	27.5	69	127	1.79
	Varnish I	27.6	68	102	1.78
	Varnish I	28.7	68	139	1.84
News B	Varnish I	29.5	69	175	1.85
	Min. oil	29.6	69	192	1.80
Coated B	Varnish I	30.0	63	179	1.68
	Varnish I	29.9	63	190	1.62
English Finish A	Varnish I	28.8	44	103	1.25
	Min. oil	29.1	44	124	1.30
	Min. oil	30.4	43	109	1.20

From the data it appears that the paper will rupture if the impact load exceeds a maximum, irrespective of the varnish or oil. This maximum is a constant for each paper at a given temperature and humidity and may be determined directly by means of the rolling cylinder tackmeter.

From Chapter III it appears that for the tack energy density at a

peripheral roller speed V for a liquid of viscosity η, the following relation holds:

$$D_V = 142V \times \eta^{3/2} \tag{30}$$

Correspondingly, for $D_V = D_r$, at the rupturing velocity, the equation

$$D_r = 142V_r \times \eta^{3/2} \tag{42}$$

is valid.

If D_r has been established for a given paper at a given temperature and humidity, the minimum web speed which will produce rupture may be calculated for a given ink of a given plastic viscosity. Conversely, the minimum viscosity of an ink which will produce rupture may be calculated from the above equation for any given web speed.

D. MECHANISM OF PICKING

Conventional views indicate that paper rupture should occur when the paper is the weakest link in the paper-ink-plate union formed by the printing pressure and separated upon being subjected to stress. According to these views, the break is generally expected to occur in the ink, but for very tacky inks at higher speeds the paper may rupture.

Experimental evidence shows that this picture is erroneous. In this experiment, carried out by means of the rolling cylinder tackmeter, a cylinder covered with a nonabsorbing paper was passed at high speed over a plate covered with a viscous ink, causing paper rupture. By inking the cylinder and covering the plate with paper, the identical effect was shown. When, however, the cylinder was rolled over a plate covered with inked paper, no rupture at all occurred. When half of the paper on the plate was inked, as in the previous experiment, while the other half of the cylinder was inked, the part of the paper corresponding to the inked part of the cylinder ruptured, leaving the rest of the paper intact, even when using a very viscous varnish at the highest possible roller speed. According to conventional views the paper, in all cases being the weakest link, is expected to rupture in all instances, in complete contradiction of the experimental facts.

The process of film separation cannot be considered statically, since the behavior of an ink film under impact differs basically from its static reaction. Likewise, as shown extensively by Anderson and

Steenberg,[7] paper reacts quite differently under impact from under static stresses. Paper rupture in the printing process must be considered to occur when the energy density of the impacting wave exceeds the rupture energy density of the paper.

Upon film separation an oscillatory disturbance will extend from the place of contact of ink and paper, in the ink film as well as in the paper, vibrations being created in both media. Rupture may then occur either in the ink film or in the paper, depending upon the magnitude of the rupture energy density of the paper and of the tack energy density of the ink.

In the last of the experiments described, where the cylinder was rolled over inked paper, the impact took place in the interface between metal and ink. The wave, therefore, was propagated in the metal and in the ink. Damping occurs in the ink film and the vibrational disturbance is either dissipated completely or greatly weakened at the paper-ink interface. Therefore no rupture of the paper was expected and none occurred, in complete agreement with the vibrational theory.

[7] O. Anderson and B. Steenberg, *Svensk Papperstidn.*, *53*, 1 (1950).

CHAPTER XV

OFFSET

Offset is an undesirable manifestation of the interaction between ink and paper. It is caused by an uncontrolled secondary ink transfer, from one part of the printed sheet, directly or indirectly, to another part.

The simplest form of offset results from ink transfer due to the pressure of folding, binding, bundling, or stacking, from an incompletely set ink to another surface with which it is in direct contact. This form of offset occurs when the speed of printing is too high for the setting period required to permit handling of the printed sheets or web. A particularly objectionable form of offset is found in the sticking together of sheets which have been stacked in a pile, an extreme case of which is blocking, the cementing together of the sheets in a solid mass. The use of anti-offset sprays eliminates offset to a certain extent, but is ineffective at higher speeds. Such sprays act to prevent a direct contact between the printed sheet and the next sheet by spraying an evaporating solution of a gum, a solidifying liquid, or a dry powder on top of each printed sheet.

A particularly conspicuous form of offset is so-called first impression offset. It occurs when a paper is printed on two sides in a single operation, the second impression being made while the first impression has not completely set. It is one of the major problems in newspaper printing. At press speeds of 1200 ft. per minute, for instance, at a distance of 2 ft. between impression cylinders, the time required for the web to travel from the first to the second impression cylinder is only one-tenth of a second. Since in conventional newspaper printing the ink does not set in so short a time, part of the wet ink is transferred to the second impression cylinder which is rapidly covered with an ink film in the pattern of the first plate cylinder. During the printing of the second side the pressure from the second plate, exerted through the web, will cause transfer of ink from the second impression cylinder to the first printed side. The offset is formed in the pattern of the second plate and might therefore be

mistaken for print-through. The fact that this form of offset also occurs when the second form is not inked at all proves it is different from print-through. As discussed before, microscopic observation will reveal the difference between show-through and offset, while offset, contrary to show-through or strike-through, may be removed with a rubber eraser.

First impression offset is observed predominantly in the middle tones of halftone reproductions. This is due generally to the fact that halftones have a relatively high degree of inking per unit area and thus contribute heavily to offset on the second impression. The effect naturally is not visible on solids and, through lack of inking, is equally invisible in the highlights.

If the high-speed printing process could be controlled exactly, halftone dots of the first impression offset would be superimposed precisely on the halftone dots of the first impression. This would lead to local color intensification due to double printing and therefore would be rather undesirable. Actually, however, a perfect register is rarely accomplished in newspaper printing, and the effect of dots which are not superimposed on the original dots is marked. It is often intensified by the moiré interference pattern of the dots. Figure XV–1 shows first impression with halftone dots superimposed on those of normal printing, and Figure XV–2 an enlargement of the central section. Figure XV–3 shows first impression offset with dots in adjacent spots, while Figure XV–4 shows an enlarged central section. Finally, Figure XV–5 shows an example of first impression offset (on map) and show-through (outside of map) of the same lettering.

The basic cure for first impression offset is to prevent the inking of the second impression cylinder. This was done in earlier methods of perfecting printing by placing an absorbent paper web, a so-called traveling tympan, between the second impression cylinder and the web. A more acceptable solution of the problem is found in the use of fast-drying inks, such as heatset or moisture set inks in magazine typography or rotogravure in weekly newspaper printing. A proper web tension, a medium printing pressure, and moderate inking will reduce first impression offset to some extent. The use of tympan sheets which show a reduced ink receptivity, such as those

[1] I. M. Bernstein, *Am. Ink Maker*, *24* (9), 49 (1946).

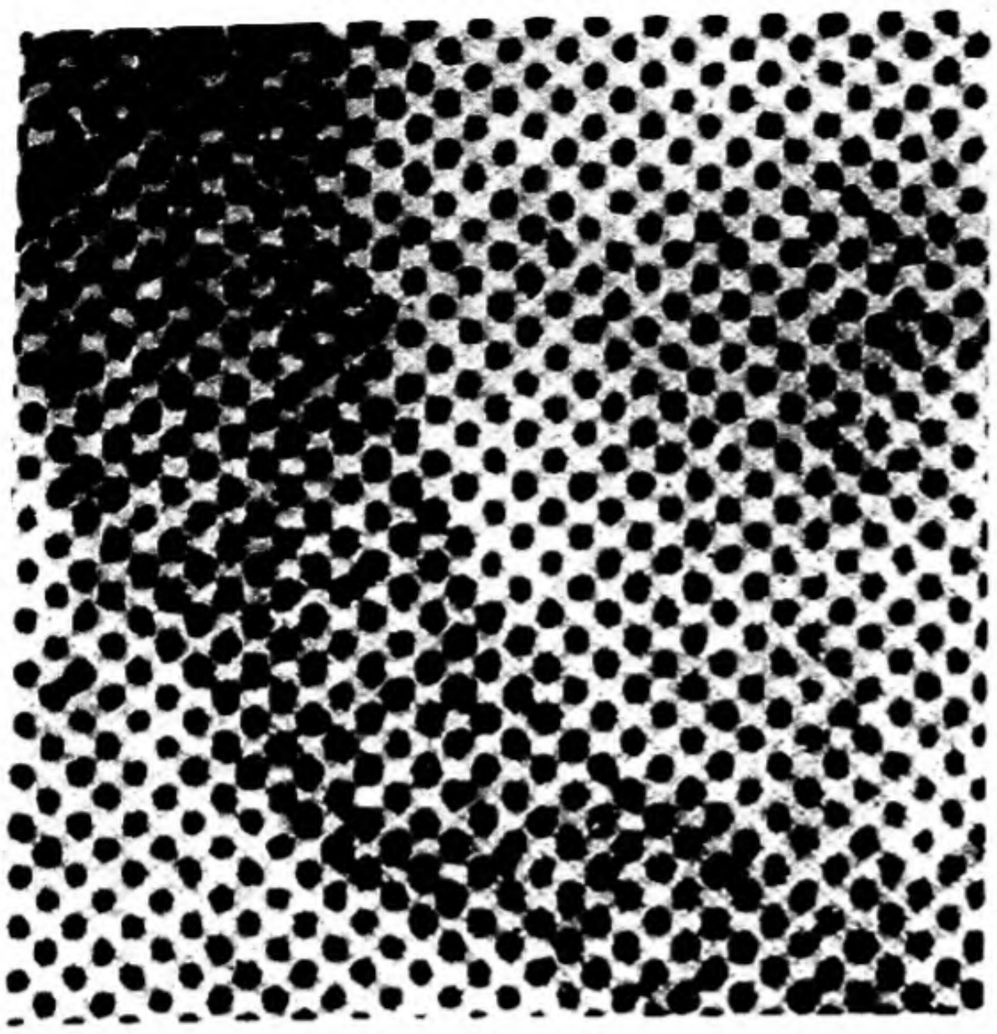


Figure XV-1. First impression offset with superimposed dots.[1]

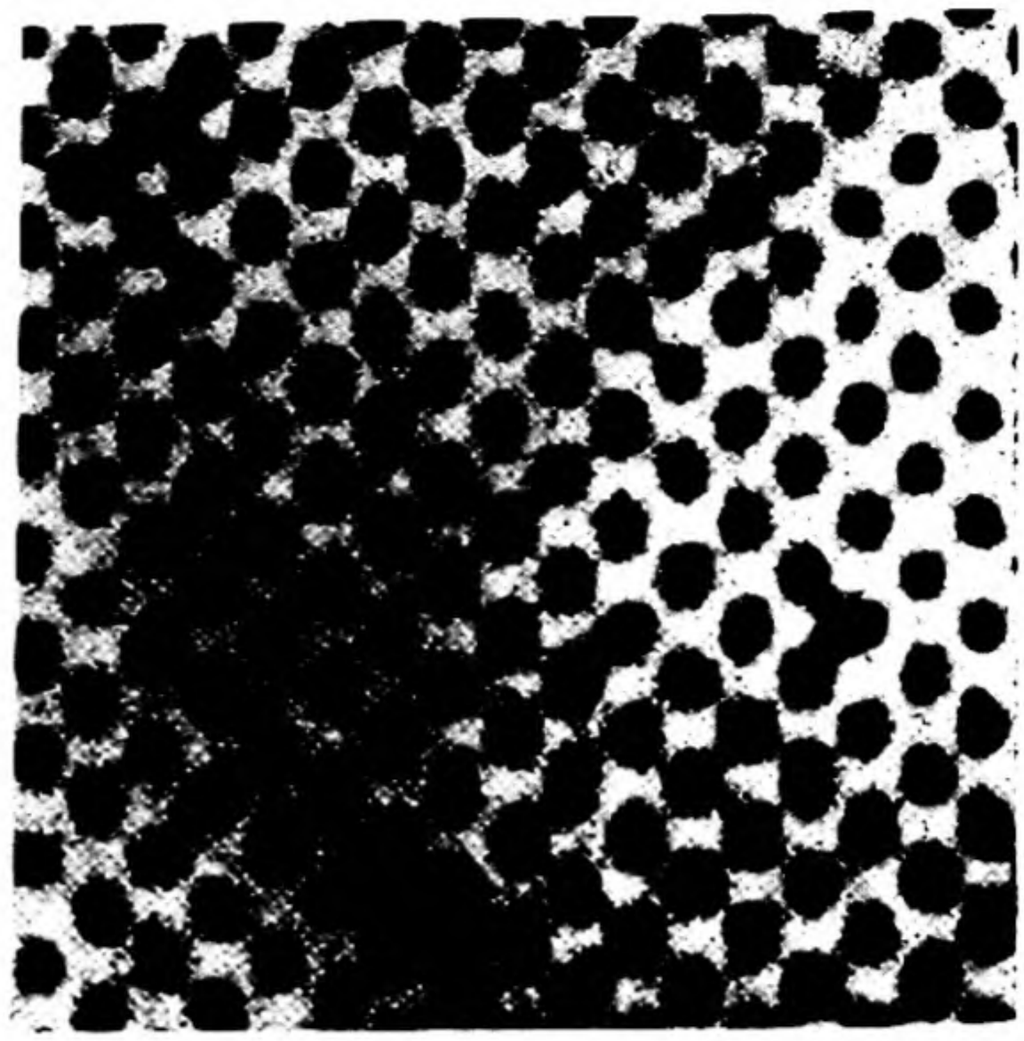


Figure XV-2. Enlarged section of Figure XV-1.[1]

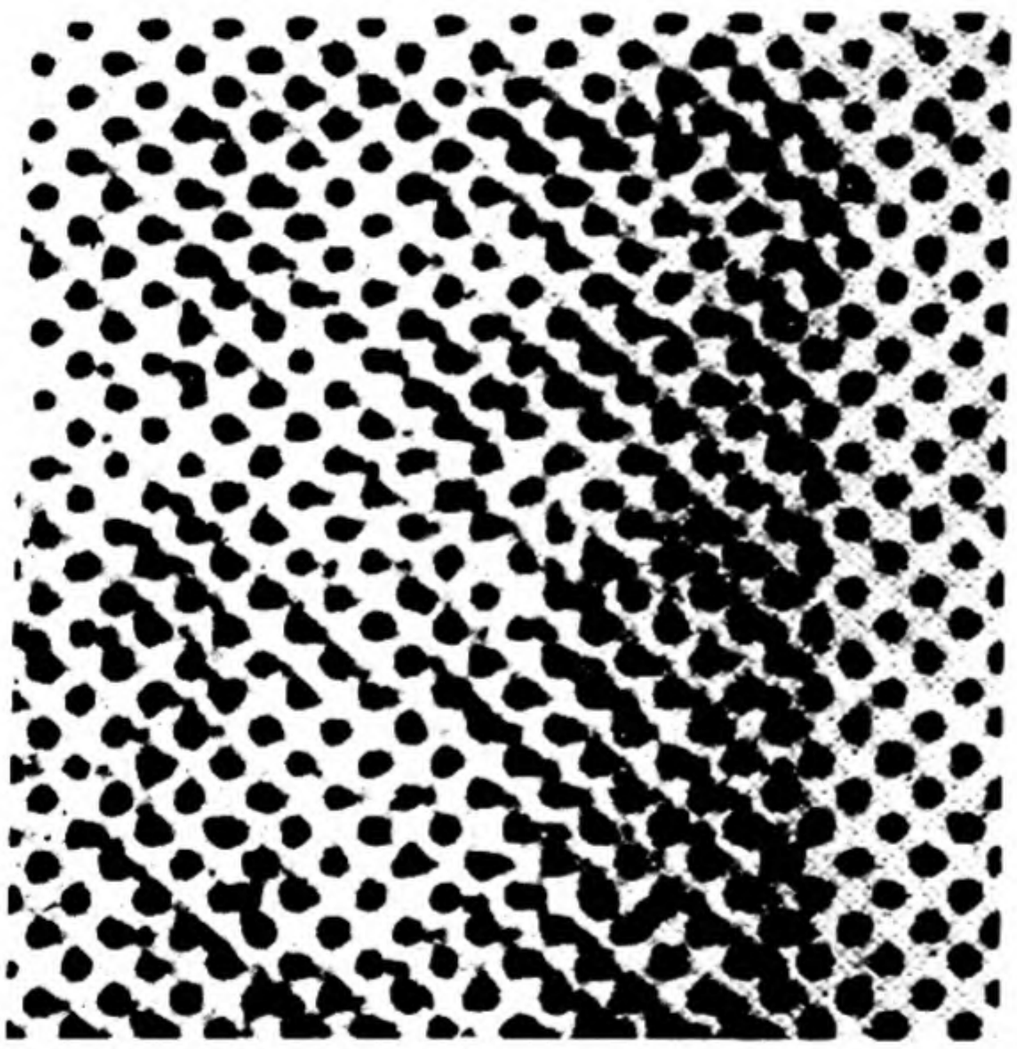


Figure XV-3. First impression offset with adjacent dots.[1]

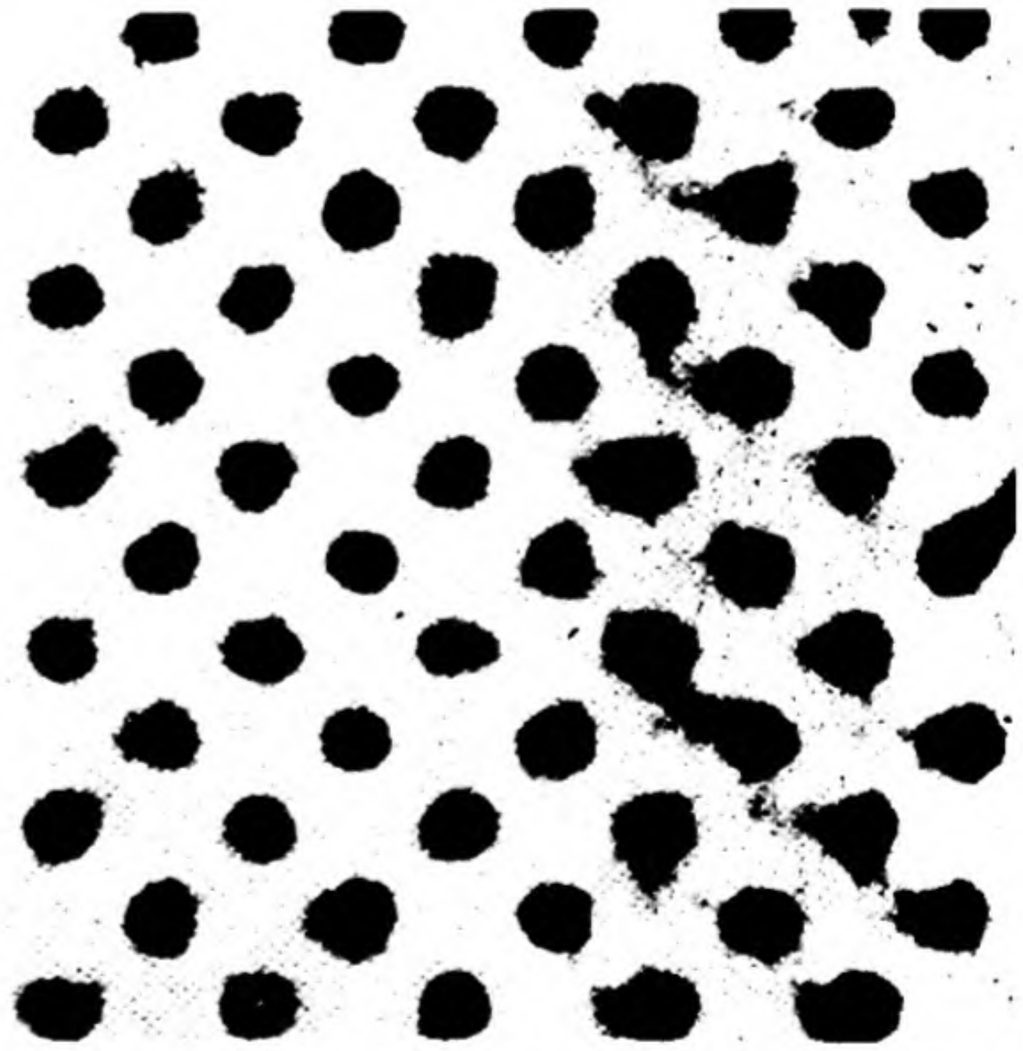


Figure XV-4. Enlarged section of Figure XV-3.[1]

in the surface layers of which glass beads are embedded, is helpful. Yet, newspaper printing is very considerably affected by this form of offset. The quality of the first impression side is always quite inferior to the quality of the reproductions on the second impression side not subject to this form of offset. In addition, the necessity of using reduced inking causes a reduction in blackness. The blackness of the

Figure XV-5. Example illustrating first impression offset (on face of map) and show-through (outside of map) of the same design.

second side is generally less than desirable in order not to show too much of a contrast between the two sides of a newspaper.

An improvement in the direction of increasing the speed of penetration of news ink is not to be expected. It was found that a greatly increased rate of penetration hardly reduced first impression offset and caused a marked increase in print-through. A real elimination of first impression offset can only be expected with another system of ink drying, such as heatset, moisture set, or coldset. In view of the exceedingly high cost of these methods and their major difficulties for newspaper printing, such a development does not in general seem economically feasible at this time.

CHAPTER XVI

PHYSICAL DRYING OF INK

A. SETTING AND HARDENING OF INK

The drying of inks on paper is a complex phenomenon. A differentiation may be made between setting and hardening in the process of ink drying.

An exact definition of ink setting is not very well possible, in view of the relative significance of the term. Ink setting is generally understood as the process that transfers a liquid ink film into a stage in which it is not affected by the mechanical handling involved in subsequent phases of the particular printing process. Thus, for instance, under certain conditions a particular ink may set satisfactorily on a given paper for a sheet-fed operation, but not for a web press. A properly set ink film, therefore, will not be rubbed off, set-off, or otherwise transferred or damaged during the following operations.

Ink hardening is the process of the change of the ink film from the semi-solid "set" stage into the completely dried ink film which has reached its final stage. Inks may show pronounced differences in hardness and resistance to abrasion or to chemicals, but the hardened ink in each case has reached the end of its chemical or physical conversion, not counting, of course, the slow process of film deterioration characteristic of oleoresinous films.

Inks also show marked differences in their setting as well as in their hardening times. Certain inks never reach any appreciable degree of hardening. In other inks setting and hardening follow one another so rapidly that they are hardly recognized as separate stages. In still others no definite setting or hardening stage is observed at all. In discussing the influence of ink and paper in the process of ink drying, it is advantageous to review each class of inks separately.

B. DRYING BY ABSORPTION

The essential characteristics of the process of ink drying by absorption have already been treated previously as part of the dis-

cussion on ink penetration into paper. The inks are all pigment dispersions in relatively inert vehicles, while the paper stock is absorbent to allow a rapid vehicle penetration.

Although it is apparent that the printing pressure initially causes a marked vehicle penetration, the remaining vehicle-pigment "plug" is by no means set. This lack of setting immediately after printing is the cause of first impression offset in newspaper printing, as discussed in the preceding chapter. After the impression, more vehicle is withdrawn from the ink plug by the capillary forces of the paper, counteracted, however, by similar forces in the ink plug. An equilibrium is finally reached in which some vehicle remains embedded in the pigment, even after a prolonged period of time with a non-evaporating vehicle. It appears that in black news inks and in inks with organic pigments the affinity of the usually polar paper fibers for the nonpolar mineral oil vehicles used is not greater than the affinity of the vehicle for the pigments. The ink plug, therefore, contains appreciable quantities of vehicle in the equilibrium condition, and the ink never hardens in the usual sense. For this reason, inks drying by absorption never have any resistance to abrasion. In the absence of any hardening, the fact that the pigment is retained at all by the paper must be ascribed to a mechanical adherence, by which the superficial paper fibers retain the pigment particles.

If low-viscosity polar vehicles are used, a marked affinity is noticed between the polar paper fibers and the vehicle. With liquids such as water, alcohols, formamide, and like materials, therefore, the liquids penetrate into the paper fibers, while nonpolar hydrocarbons only penetrate into the interstices between the fibers. With polar liquids the equilibrium of the vehicle partition between paper and pigment plug is essentially reached when most of the vehicle is withdrawn from the pigment. In many instances, however, such liquids are volatile and disappear completely from the film by evaporation.

Inks drying by absorption are always printed on absorbent stock. When printed on nonabsorbent stock they simply do not set at all.

C. DRYING BY EVAPORATION

Various types of ink dry by evaporation. Rotogravure inks, in addition to all water and alcohol based inks, are "low-temperature" evaporating inks. Heatset inks evaporate in a marked degree only at

elevated temperatures. While part of the pigment-vehicle separation occurs by penetration, the major drying in these inks always takes place by evaporation.

The most important factor determining the rate of evaporation of the ink is the solvent. The simplest case is that of a solvent composed of a single component. The evaporation rate of the solvent is then a constant determined by the physical characteristics of the solvent. A number of conditions determine the actual quantity of liquid evaporated during a certain period of time. It was found that the evaporation rate is a function of vapor pressure and heat of vaporization at the liquid temperature, the difference in temperature between evaporating liquid and the air above the surface. the velocity of the air stream past the surface, the thermal conductivity of the air, and the area of the surface.[1]

In actual practice, as a first approximation of the evaporation rate, one may rely upon a comparison of the boiling points at the same pressure for solvents belonging to the same class of materials. The higher the boiling point, the lower the vapor pressure and the lower the evaporation rate of the solvent. If, however, the materials do not belong to the same class of chemical components, the boiling points generally do not give a satisfactory indication of their rates of evaporation, since the vapor pressures at any given temperature are not necessarily in line with the boiling points.

A more exact determination of the evaporation rate is carried out in a complicated apparatus[1, 2] requiring a closely regulated constant supply of heat which is in turn dependent upon the temperature of liquid and air and on the total evaporating surface, as well as on the thermal conductivity and the film thickness of the liquid. In addition, a constant stream of air of constant temperature and humidity and of controlled flow rate has to be maintained across the surface of the evaporating liquid.

A simpler method is to determine a relative rate of evaporation with respect to a standard liquid, for which toluene is generally used. The evaporation rate under the simplified conditions is first determined for toluene. The rates for the other liquids may then be deter-

[1] L. S. Galstaun, *ASTM Bull.* No. 170, December 1950.
[2] I. A. Wetlaufer and J. B. Gregor, *Ind. Eng. Chem., Anal. Ed., 1,* 290 (1935).

mined under identical conditions and expressed as a percentage of the toluene rate.

A conventional simplified apparatus for the measurement of solvent evaporation consists of a Jolly spring balance with a small pan attached to the end, on which a given weight of solvent is left to evaporate. The balance is surrounded by a Pyrex glass column acting as a chimney. Heat is supplied at the bottom by an electric bulb. The loss of weight by evaporation with time may be determined in milligrams per minute under the conditions of the experiment and expressed as a percentage of the toluene evaporation rate under identical conditions. For example, it was found that the relative evaporation rate of benzene is 288 and of xylene 34, both with respect to toluene.

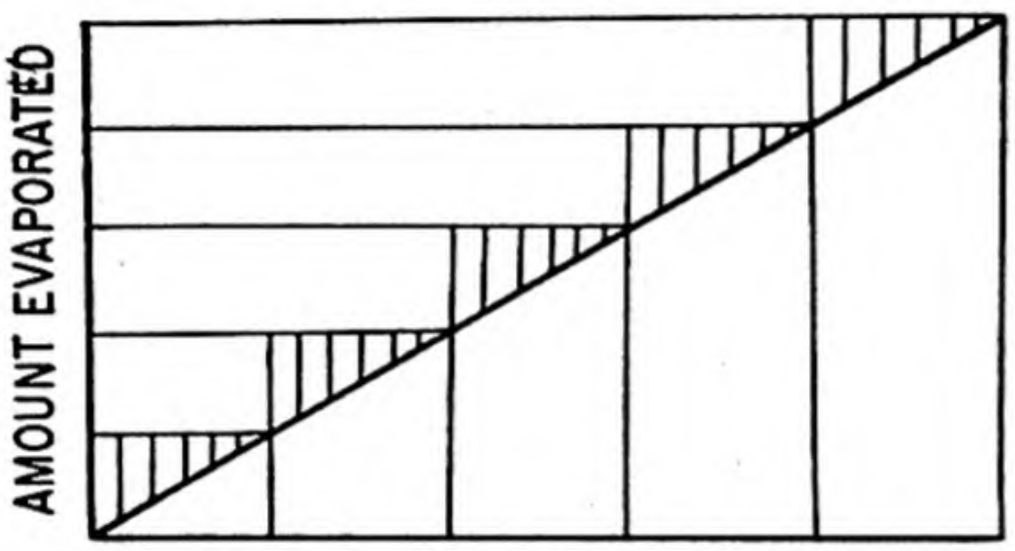


Figure XVI-1 Evaporation of a liquid with constant boiling point.

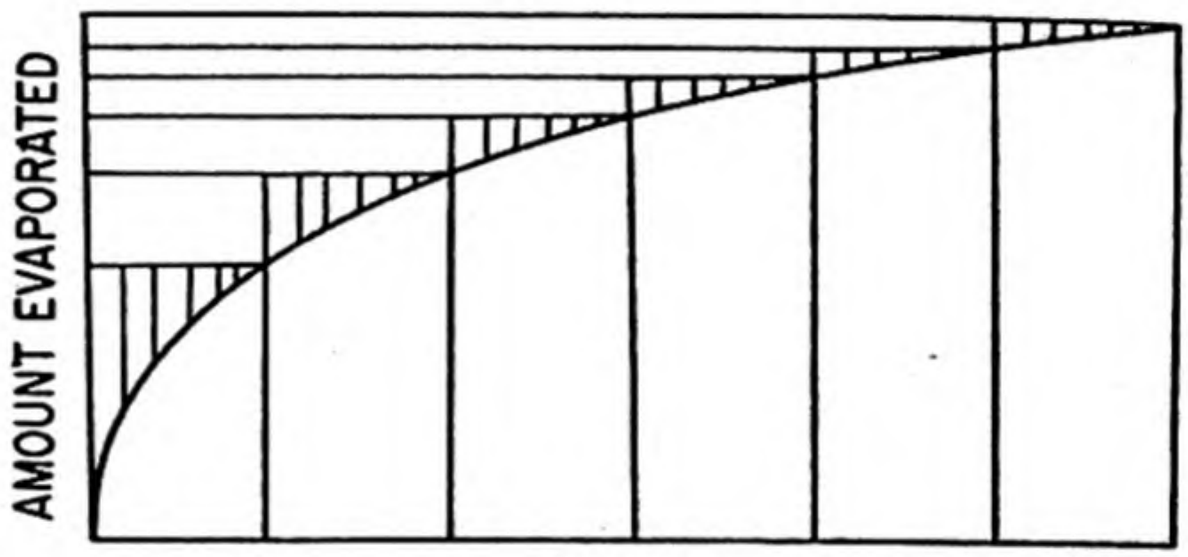


Figure XVI-2. Evaporation of a liquid with a boiling range.

A simplified method of calculating the evaporation rate of liquids consisting of single compounds has recently been developed.[3] It was found that the relative evaporation rate E_r may be expressed by the equation

$$E_r = \frac{V_{25} \times M \times 1.64}{d_{25}} \tag{43}$$

in which V_{25} is the vapor pressure at 25°C., M the molecular weight, and d_{25} the density of the liquid at 25°C. The constant of 1.64 was derived from evaporation data of toluene, where E_r was arbitrarily set at 100, as indicated previously.

In practical printing the evaporating liquid is usually not a simple chemical compound, but consists of a mixture with a boiling range such as is found in most hydrocarbon solvents of petroleum origin. During the process of evaporation the composition is con-

[3] *Industrial Solvent Naphthas,* Socony-Vacuum Oil Company, Inc., 1946.

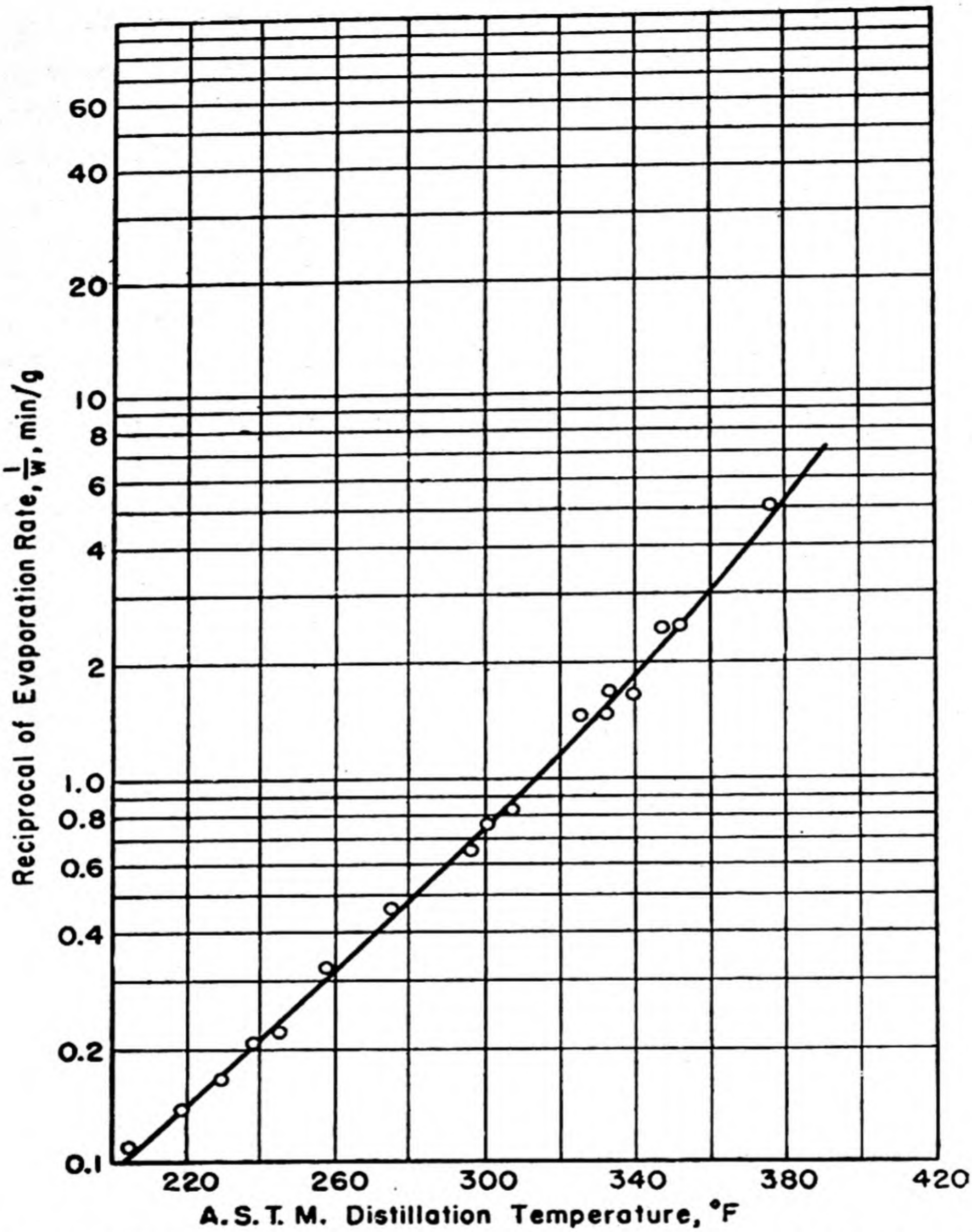


Figure XVI-3. Correlation between rate of evaporation and A.S.T.M. distillation temperature for hydrocarbon liquids.[1]

stantly changing, since the most volatile parts of the liquid escape first. Consequently it is not very well possible to establish a single evaporation rate. This behavior is illustrated in Figures XVI–1 and XVI–2.[3]

For a single liquid or for a constant boiling mixture (Figure XVI–1) equal amounts of solvent evaporate in equal time intervals.

as indicated by the shaded areas. Figure XVI–2 indicates the same relationship for a mixture with a boiling range. It appears that smaller and smaller amounts of solvent evaporate in equal time intervals, in view of the reduction in vapor pressure caused by the initial evaporation of the most volatile parts of the solvent.

It was found by Galstaun[1] that for a mixture of hydrocarbon solvents the average evaporation rates for each fraction plotted on a logarithmic ordinate against the A.S.T.M. distillation temperatures show a linear relationship for all practical purposes as indicated in Figure XVI–3.

Equation (43), though strictly valid only for single liquids, may be advantageously used in first approximation for mixtures. The factor M then indicates the average molecular weight for each fraction considered.

Evaporating inks, like other inks, generally consist of a vehicle and a pigment. The vehicles are made up of a solvent and a resinous binder, the latter comprising often as much as 70 per cent of the vehicle. It is therefore not surprising that the influence of the resinous binder on the solvent evaporation rate is pronounced. Generally dissolved materials reduce the vapor pressure of the solvent and therefore reduce the evaporation rate. It appears that the more soluble resins have a greater reducing effect on the rate of solvent evaporation.

TABLE XVI–1

Solvent Evaporation of Resin Solutions

Resin	Rate of solvent evaporation, mg./cm.^{2}/min. at 200°C.
Phenolic	3.10
Limed rosin	2.94
Petroleum resin	2.80
Polymerized rosin	2.45

Table XVI–1 shows these differences for vehicles consisting of 70 per cent resin and 30 per cent petroleum solvent.

A secondary effect of the resinous binder is that a minor fraction of the solvent may still be found in the film even after a prolonged period of time. This solvent retention causes plasticization of the

film, resulting in soft, tacky, often undesirable films which have a tendency to cause offset. It was observed that hydrocarbon resins may retain as much as 10 per cent of an aromatic solvent. Generally the better soluble a resin is in the solvent, the more solvent is retained in the film. To promote a speedy solvent release it is essential to combine resins with solvents which do not show a high solubility in the solvent. On the other hand, lack of solubility may cause initially a very high viscosity, followed by gelation or even precipitation.

Both the concentration as well as the character of the pigment influence the evaporation rate of the ink. In addition, the particle size of the pigment used has an important bearing on the rate of solvent evaporation.

The influence of the concentration is demonstrated in Table XVI–2, where are given the rates of solvent evaporation of a petroleum

TABLE XVI–2

Pigment Contents and Rate of Solvent Evaporation

Per cent black	Rate of evaporation, mg./cm.²/min. at 200°C.
0	3.54
5	2.21
10	2.01
15	1.78
20	1.51

solvent at 200°C. in the presence of a hydrocarbon resin and varying quantities of a channel black.

The influence of the type of pigment is shown in Table XVI–3, where the evaporation rates are indicated for a 10 per cent by weight dispersion of pigments in a vehicle consisting of a hydrocarbon solvent and a limed rosin binder.

In general, the lower the specific gravity, the lower the solvent evaporation rates. For equal specific gravities the greater effect is found with the smaller particle sizes. When a clay pigment was separated into three fractions, the largest particle size clay readily released the solvent. The medium fraction was somewhat slower, while the smallest particle size fraction showed a much slower rate of evaporation.

While the major effect on the rate of evaporation is due to the solvent, important secondary effects are caused by the resin and the pigment, both dependent on the type and the concentration.

From the above it appears that a single compound solvent has the most advantageous characteristics of evaporation in showing a single rate of evaporation. The ink maker using a solvent mixture, such as a petroleum fraction, will always strive to obtain a close-cut fraction, resulting in a solvent with properties resembling those of a single compound liquid. Wide cuts will show initially too rapid a rate of evaporation and may have a slow end point, resulting in a considerable quantity of solvent being retained in the film in actual printing. often the cause of offset and other undesirable manifestations oi tacky films.

TABLE XVI–3

Pigment Type and Rate of Solvent Evaporation

Pigment	Sp. gr.	Av. particle size, millimicrons	Solvent evapn. rate, mg./cm.²/min. at 200°C.
Channel black	1.77	30	1.81
Monastral blue	1.51	65	1.75
Chrome yellow	5.90	210	3.49
Lithol red	1.59	90	3.25

Certain higher molecular materials, such as lignin, do not retain the solvent at all, but rapidly become nontacky films when formed from evaporating liquids.[4] Their use in evaporating solvent types of inks has therefore some advantages over the conventional low-molecular resins. The choice of available materials, however, is greatly restricted.

Heatset inks have become more and more important for publication printing until now most of the national magazines have adopted this system. Heatset lithographic inks have become a commercial reality, although for general application the major difficulties seem to be in securing a proper paper stock.

The petroleum type of solvents used, generally boiling between 200–270°C., requires flame ovens, steam drums, or hot air for a complete ink setting between impressions. As a result of the heat applied,

[4] A. Voet, U. S. Patent 2,525,433, Oct. 10, 1950.

there is a considerable weakening of the paper, causing excessive web breaks and generally reduced resistance to mechanical handling. Improved inks, requiring less heat for setting, are highly desirable. To meet the need svstems with a plurality of solvents, where precipitation takes place before complete evaporation of the solvent, are in the development stage.

A new approach using a plurality of solvents, originated by Time, Inc., has resulted in the formulation of inks, at present in an experimental stage, known as "balanced inks." After the evaporation of part of the more volatile solvent components a separation into two liquid phases occurs. One of the liquids has a low viscosity, while the other, containing nearly all the pigment and binder, has a high viscosity. The low-viscosity phase penetrates into the paper, while the second phase dries rapidly to a glossy film. Balanced inks of this type require less heat to set and dry than conventional heatset inks, since a complete evaporation of the solvent is not required. Only a fraction of the vehicle is evaporated—enough to cause the "unbalance" resulting in phase separation. When made with a mixture of glycols and hydrocarbon solvents, however, the inks are extremely sensitive to moisture.

This system actually combines several physical methods of drying. Besides evaporation and penetration as essential parts, there is also phase separation. The unusual part is that separation does not occur in a solid and a liquid phase, such as is found in the precipitating inks. but that two liquid phases are formed.

Mechanical improvement of presses, with a more compact, enclosed ink distribution system, would be helpful in permitting the use of inks with more volatile solvents.

In heatset printing the web may reach temperatures as high as 250–300°C. At these temperatures the resinous component of the vehicle remains fluid, even after a complete evaporation of the solvent. The resulting appreciable penetration of the fluid resin into the paper stock is the cause of the formation of a flat, lusterless finish. Where glossy prints are required, excessive resin penetration at high temperatures has to be prevented. This may be done by using complex vehicles in which an insoluble gel has been colloidally dispersed. The gel particles do not dissolve in the vehicle at the highest temperatures reached and are filtered off, while the rest of the vehicle penetrates

into the paper, resulting in a glossy film. Gels of a similar type were developed during World War II as the "gelled gasoline" for incendiary bombs, such as Napalm and like materials. They consist of metallic soaps, such as aluminum palmitate, stearate, or octoate. They are used extensively in gloss heatset inks.

D. DRYING BY SOLIDIFICATION

Drying by solidification is basically the simplest of all drying processes. Coldset inks are made to be printed at temperatures above their melting points. Because they cool rapidly when printed on a cold paper stock, there is a speedy solidification of the molten ink. Coldset inks are suitable for letterpress and gravure printing. They are usually printed at 105–110°C. and are made to solidify at 75–80°C.

Coldset inks have a number of characteristics different from other inks. They do not penetrate into the paper, because the molten ink cools so rapidly after touching the colder paper that its viscosity becomes too high to be absorbed by the stock. Yet an excellent adhesion between ink film and paper exists. Show-through, therefore, is reduced to the mere paper transparency, and strike-through is nonexistent in coldset inks.

Another advantage of coldset inks is that there is very little dot distortion, again on account of the rapid change in viscosity of the fluid ink after contact with the paper. As a result, it appears quite feasible to print a 133-line halftone screen in high-speed newspaper printing on news stock. In addition, the type is clearer owing to sharp contours and the nearly complete absence of irregular sideways ink displacement.

Because coldset inks set rapidly, first impression offset is eliminated. A water-cooled roller to aid in cooling is, however, desirable in high-speed printing. Since there is a protective film around the pigment, no rub-off, as experienced in conventional newspaper printing, is found in coldset inks.

The inks are made from a mixture of resins, waxes, plasticizers, and like materials in which a pigment is dispersed. As a result of this composition, a real hardening to a tough film never takes place. Coldset ink films are therefore not resistant to abrasion, but are subject to marring by strong mechanical handling, although improved formulation may remedy this failure to some extent. This lack of abrasion

resistance, however, is not a serious objection in many applications. The major difficulty encountered in printing with coldset inks is of a mechanical nature. The requirement of uniform heating of existing presses necessitates extensive changes, to allow a circulating hot water system to heat fountains and cylinders.

From actual experience it appears that conventional newspaper presses built to run at room temperatures do not expand uniformly when heated to about 110°C. Consequently press wear is excessive and, in addition, roller and blanket wear is very great, as a result of the inability of most types of natural or synthetic rubbers to stand up to the molten inks at higher temperatures for prolonged periods of time.

It is evident that the many advantages of coldset inks do not outweigh the major technical difficulty of their application, and, therefore, after a prolonged period of testing, the coldset process was abandoned in newspaper printing. On the other hand, the excellent results that have been obtained seem to make it technically desirable to build a special press, designed to run at the elevated temperatures required by the coldset process. The economic possibility of such a press depends on a number of factors which cannot be properly evaluated at this time.

E. DRYING BY PRECIPITATION

The principle of drying by precipitation involves the interaction between the ink vehicle, consisting of a binder and a solvent, and a diluent. The diluent is miscible with the solvent in all proportions, but the vehicle does not tolerate more than a limited quantity of diluent. If this limit is surpassed, the binder precipitates. In a satisfactory precipitation ink the binder precipitates in a film which rapidly becomes continuous.

Historically the first examples of precipitation inks were the wax set inks. Inks of this type suitable for letterpress printing consist of a pigment dispersed in a vehicle composed of a solution of nitrocellulose in a high-boiling solvent. Upon immersing the wet print in molten wax, the binder precipitates and forms a hard, smooth, protective film. Wax set inks, however, are suitable only for those prints which have to be coated with wax, such as bread wrapper inks, milk bottle top inks, and similar waxed packaging materials.

The most important group of moisture set inks depend for their setting on the incompatibility of the varnish with excess of water. The solvents employed, which must be completely miscible with water in all proportions, are usually polyglycols, such as diethyleneglycol. In addition, solvents such as 2-methyl-2,4-pentanediol, propyleneglycol, butyleneglycols, glycerol acetates, and like materials are used.

The resinous compounds applied are chosen for their ability to tolerate a limited quantity of water without any precipitation, but to precipitate immediately as soon as the limit of tolerance is surpassed. For instance, rosins are undesirable, since their water tolerance is very limited, which will cause precipitation of the ink on the rollers of the press at a somewhat high relative humidity. Cellulose derivatives, used originally, also have too low a water tolerance to be practicable in moist weather.

The more desirable resinous binders have a high enough water tolerance to be printed at the highest relative humidity without precipitation on the rollers of the press. The most important representatives of this group are the maleic and fumaric modified rosins, obtained by means of a Diels-Alder condensation of rosin with the respective acids or with maleic anhydride. These resins, while of a light color, have a high acidity (acid number of about 350). They are therefore rather reactive with a number of pigments, so that the choice of pigments usable with them is somewhat limited. Other resins which have a suitable water tolerance and which are not so strongly acidic have been developed. They are predominantly of the phenolic type. Prolamines such as zein are often used, in addition to resins, to impart toughness and flexibility to the film of the binder.

For darker inks a rather unusual material, known as beta naphthol still residue pitch, a residue from beta naphthol manufacture, appears to have the necessary characteristics for moisture set inks. Another suitable, dark-colored binder is lignin, produced as a waste material in the soda or sulfate paper manufacturing process. An additional suitable resinous material for water set inks is the rosin fraction, known as "Vinsol," which is insoluble in hydrocarbon solvents.

The ability of a varnish to tolerate water may generally be determined by means of a simple titration. Water is added slowly to an

agitated known quantity of varnish until precipitation occurs. In another version of the test a mixture of water and a glycol are added slowly to the agitated varnish until separation of the liquid into two layers occurs.

The water tolerance is an important characteristic of a moisture set ink. Inks with too low a water tolerance cannot be used in a moist atmosphere, while inks with too high a water tolerance do not set properly with steam or water. The water tolerance of inks may be modified by addition of materials, such as amines, greases, and waxes. It is more advantageous, however, to prepare inks with the more desirable water tolerance by using the proper mixture of resins of different water tolerance.

Water may be taken up from the paper or from the atmosphere or may be artificially added as a spray of water or a jet of steam. Kraft papers, which often contain as much as 8 per cent or more of moisture, do not as a rule require a water or steam treatment to cause ink precipitation. The initial set is caused by the water which is present in the paper. Complete precipitation usually occurs quite rapidly by water absorption from the atmosphere.

Since no auxiliary equipment is needed for the setting of moisture set inks on Kraft paper, these inks are being used extensively for bag printing. Other papers require a treatment with finely divided liquid water or with steam. After precipitation of the resin, the mixture of solvent and water quickly penetrates into the paper fibers as a result of the polar characteristics of both solvent and diluent. The liquids are finally eliminated from the paper by evaporation.

Moisture set inks are completely odorless and do not exhibit any odor even during the process of setting, unlike most inks based on drying oils. In addition, since no toxic materials are present in the inks, there is no objection to their use as food wrapper inks. With such pronounced advantages it is not surprising that these inks have been very successful in the food wrapper industry.

Moisture set inks may be applied in publication printing, although, in view of the higher priced glycol solvents, they are somewhat less economical than the heatset inks which are based on petroleum solvents. Their use seems to be promising for newspaper printing, since mechanical requirements for the setting of moisture set inks are much simpler and the hazards involved are considerably less than those of

heatset inks. Certain difficulties, however, arise with the use of moisture set inks in publication printing. Although at low speeds a single water spray or a steam jet is quite effective to set the inks, at much higher speeds an air blanket travels with the web and is held tenaciously, preventing direct contact between the printed film and the water or steam. The air blanket is penetrated only by means of the slow diffusion process of water vapor. In order to effect a proper setting at high speeds it is desirable to direct a jet of superheated steam at a pressure of 5–10 p.s.i. through fine nozzles close to the surface of the paper web. The construction of several rows of these nozzles enclosed in a steam box is necessary to prevent first impression offset at web speeds of 1000 ft. per minute or over.

Another difficulty in newspaper printing with moisture set inks at higher speeds is the high affinity of the polar solvent for the paper fibers, causing a loosening of fibers from the surface of papers with a loose structure, such as newsprint. These fibers eventually cause fill-in of plate screens, especially in the middle tones. This difficulty may be overcome by the use of a more suitable though more expensive paper stock.

The successful adoption of moisture set inks in newspaper printing will primarily depend on economical considerations, since the technical difficulties are not basically a deterrent to their use. Moisture set inks do not show any first impression offset and do not rub or show print-through, but they must also be competitive with low-priced news inks based on mineral oils. Since at present it is necessary to use the more expensive glycols as the main vehicle constituents, a more general application of moisture set inks in newspaper printing is unlikely in the near future.

F. INK DRYING BY FILTRATION

Filtration inks differ from conventional inks in the structure of the vehicle. In conventional inks the vehicle is entirely, or nearly entirely, a homogeneous liquid. In filtration inks, however, the vehicle is a colloidally dispersed system. The solid vehicle fraction, usually of a resinous or rubbery nature, is dispersed in a low-viscosity liquid in which the pigment also is dispersed. Filtration inks are therefore complex dispersed systems in which both the resinous component as well as the pigment are present in the finely divided state.

Upon printing on an absorbent stock, part of the low-viscosity vehicle component quickly drains off into the paper, leaving the pigment and the finely divided vehicle component dispersed in a much smaller volume of liquid. As a result, by gelation the ink film becomes a rapidly hardening gel.

In order to form a continuous film, the dispersed vehicle particles must coalesce. This is only possible when the particles are tacky and easily join together. Swollen resinous or rubbery particles show this behavior. If, however, the particles lack the necessary tack to join together in a continuous film, heat has to be applied. For instance, dispersed particles of vinylites generally coalesce only at elevated temperatures, unless "tackified" with the proper plasticizers.

The principle of filtration inks, described as early as 1939,[5] has been applied for various types of inks suitable for different stocks. Of great importance is the particle size of the dispersed binder. Vehicles with particles of an average size of 0.5–1.0 micron are suitable for a coated stock, since they are filtered off while the rest of the vehicle penetrates into the coat. On a poorly absorbent stock the vehicle penetration is so slow that filtration does not occur and the ink does not show any quick-setting properties. Vehicle particles of the size indicated are not filtered off by the much coarser pores of newsprint, but the vehicle penetrates without separation into the paper capillaries. As a result no gelation occurs, and the ink does not show any quick-setting characteristics on newsprint. It is obvious that filtration inks, therefore, require a very specific application. They will show fast setting only on those types of paper stock for which they have been designed, while they usually are not as satisfactory on other types of stock.

Many types of dispersed vehicles have been used for filtration inks. A kerosene type of hydrocarbon solvent fraction is usually employed as the liquid vehicle compound. Materials such as highly limed rosin, highly polymerized drying oils, certain colloidal asphaltic materials, and many others are employed as dispersed vehicle components.

A most successful type of filtration ink, originally known as "wink-dry" ink, is made from cyclized rubber. This material may be prepared by treating natural rubber with tin tetrachloride. Cyclized

[5] A. Voet, *Drukkersweekblad*, p. 130, March 4, 1939.

rubber and materials with similar properties are marketed under the trade name of Pliolites. Pliolite-based inks usually have a kerosene cut as the dispersing medium to which aromatics are sometimes added. This material penetrates rapidly into the coated stock, causing ink setting by gel formation often within a minute after printing. Prints are then hard enough to withstand mechanical handling and may be printed on the reverse side almost immediately after the first impression without fear of offset or smudging. The ink film is hard enough to be completely resistant to abrasion within a few minutes after the impression. When printed on a stock other than a coated sheet, however, separation by quick drainage does not occur and drying proceeds more slowly by evaporation.

Notwithstanding many desirable properties filtration inks have found only a limited application. They are not economical in use and they do not set fast enough for high-speed printing, where the time between impressions is not more than a few tenths of a second. They have the additional disadvantage of showing a profound misting at higher speeds, no doubt on account of the elastic character of the binder which results in the formation of very long filaments on the press, showing many plural breaks upon separation. The use of a combination of a resinous and rubbery binder reduces the misting, but it also reduces the quick-setting characteristics of the inks.

Inks based on low-viscosity hydrocarbon oils require the use of composition rollers, which are not suitable for high-speed printing. In the absence of aromatics, rollers of solvent-resistant synthetic types of rubber may be employed. Most of the conventional rollers cannot be used with these inks, and the rubber blanket in offset printing makes their use in offset lithography very difficult. These restrictions, combined with the fact that Pliolite-based inks are high priced and are satisfactory only on coated stocks, have limited their application materially.

The principle of filtration inks has been applied successfully in many types of gloss inks. Gloss is obtained in inks when the resinous vehicle prepared on a drying oil base does not penetrate too deeply into the stock before it is set. This condition may be obtained by using stocks which show little penetration by ink. In addition, however, very viscous nonpenetrating inks are necessary, and these are also

tacky. At higher speed picking and even complete rupture of the paper surface may occur.

An important type of gloss ink employs the principle of filtration inks by using a dispersed resinous component together with a low-viscosity dispersion medium. While the final drying in these inks occurs by means of chemical changes, the initial set and the gloss are obtained as a result of the process of filtration.

Still more complicated dispersed systems are the emulsion gloss inks which usually contain three types of dispersed particles in the medium; namely, pigments, a resinous phase, and an aqueous phase. The finely divided water particles wet the paper fibers preferentially, prevent penetration of the ink, and reduce print-through markedly. They evaporate rapidly from the film after printing and a continuous, glossy, water-free film is formed from the emulsion gloss inks. Emulsions of this type always are of the water-in-oil type, the oily phase being the continuous phase. The formation of such emulsion inks is promoted by the use of cationic wetting agents, usually amines or their derivatives, in which the surface-active group has a positive electric charge.

CHAPTER XVII

CHEMICAL DRYING OF INKS

A. THERMAL POLYMERIZATION OF DRYING OILS

Until the middle thirties inks based on drying oils were by far the most important group. Although they are still important, their significance since then has steadily declined.

Inks which dry by oxidation and polymerization are based on drying oils. They consist of pigments dispersed in a vehicle the characteristic constituent of which is a drying oil. Of the practically used drying oils linseed oil is the most important. Other important drying oils of vegetable origin are tung, perilla, oiticica, and soybean. More recently, synthetic drying oils of petroleum origin have been introduced, which have found a limited application. Unmodified animal oils have only a limited significance for the ink maker.

Chemical modification of vegetable drying oils has resulted in the formation of new, improved oils. As an example of such chemical modification dehydrated castor oil must be mentioned as the oldest commercially successful synthetic drying oil. Others are made by isomerization of nonconjugated less active drying oils by means of alkali or by a catalytic treatment with isomerization catalysts such as nickel-carbon, iodine, or selenium. The conjugated isomers of the triglycerides of linseed oil or soybean oil fatty acids are more active, faster bodying, and faster drying than the original drying oils. The formation of Diels-Alder adducts with maleic or fumaric acid, carried out to upgrade linseed oil and soybean oil, has resulted in a new, superior group of oils of which especially the maleinized oils have become important. Special esters, in which the fatty esters of drying oils are esterified with polyfunctional alcohols, such as pentaerithritol or sorbitol, lead to harder drying films of an improved quality. Tall oil, a mixture of fatty acids and resin acids produced as a byproduct in paper manufacture, may be esterified with glycerin and forms an economical drying oil, satisfactory for a number of applications in the printing ink field.

More recently copolymerization of blown drying oils and styrene

or its derivatives has proved successful. Thus, styrenated oils are drying oils with excellent characteristics, suitable for many applications. Copolymers of drying oils with cyclopentadiene, known as "dryfols," have proved to be versatile oils of improved drying qualities and excellent film characteristics. Copolymerization of cyclopentadiene with fish oils has not only eliminated the undesirable fish odor, but has also greatly improved the quality of the material.

Drying oils are seldom used in the raw state, as they are obtained by pressing or extraction from oil-bearing seeds, but they are purified by a process of refining. In many instances they are also heat-bodied.

The process of heat-bodying, although applied for centuries, is not yet completely understood, but significant progress has been made toward a better understanding of the fundamental process of thermal polymerization, which causes the increase in viscosity of drying oils subjected to elevated temperatures.

Analysis of linseed oil has shown that it consists of a mixture of triglyceryl esters of unsaturated normal fatty acids with eighteen carbon atoms. The active components of these esters are glycerides of linoleic and linolenic acids, which have two and three nonconjugated double bonds respectively. Nonconjugated unsaturated triglycerides are also found in soybean oil. The acids of tung oil and oiticica oil, on the other hand, comprise octadecatrienoic acids with conjugated double bonds.

Linseed oil undergoes thickening when heated at a temperature close to 300°C., after a period of induction during which hardly any changes in the viscosity of the oil are observed. It was noticed by Chatfield[1] that the duration of the induction period varies inversely with the temperature of the polymerization. In other words, the higher the temperature, the shorter is the induction period. Tung oil and oiticica oil do not show an induction period and polymerization appears to start practically immediately after the oils have reached an elevated temperature.

The induction period was recently found to be caused by the presence of inhibitors, antioxidants which retard the oxidation. Inhibition in drying oils is due to the presence of tocopherols, sterols naturally occurring in drying oils. This was proved by the fact that

[1] H. W. Chatfield, *Paint Manuf., I,* 103, 144 (1937).

synthetic triglycerides of similar structure do not show any induction period, whereas removal of the sterols from natural oils causes the oils to dry more rapidly.

A hypothesis advanced by Kappelmeyer[2] has greatly stimulated fundamental research of thermal polymerization of drying oils. Kappelmeyer presumes that isolated double bonds of the fatty acids first shift into conjugated positions, a hypothesis pronounced earlier by Scheiber. The polymerization which occurs after the isomerization is considered to be a Diels-Alder condensation between the now conjugated double bonds of the fatty acid chains, resulting in the formation of six-membered rings with side chains. In tung oil and in oiticica oil, on the other hand, where conjugation of the double bonds already exists, no shifting appears to be necessary, and polymerization sets in immediately.

The kinetics of the process of thermal polarization was studied by von Mikush[3] and also by Cannegieter.[4] It appears that the following relationship is valid for the change of viscosity with time for drying oils at a constant, elevated temperature:

$$\log \eta_2 - \log \eta_1 = k(t_2 - t_1) \tag{44}$$

in which η_1 and η_2 are viscosities at the times t_1 and t_2, while k is a constant. This relationship appears to be valid for all drying oils. The less reactive oils, such as linseed oil, show a much smaller value of the constant k than the more reactive ones, such as tung oil.

The reaction constant k is connected with the heat of polymerization Q by the well-known thermodynamic relationship:

$$d \log k/dT = Q/RT^2 \tag{45}$$

in which T is the absolute temperature and R the gas constant. On integration the following equation is obtained:

$$\log k = -(Q/RT) + B \tag{46}$$

in which B is the integration constant. Plotting log k against the reciprocal value of the absolute temperature a linear relationship is obtained. The slope of the straight line gives the value of Q/R. The experimental data fit the equation rather well. Table XVII–1 shows the values of k and Q/R for various drying oils.

[2] C. P. A. Kappelmeyer, *Paint Oil Chem. Rev., 100,* No. 1, 5; No. 4, 4 (1938).
[3] J. D. von Mikush, *Ind. Eng. Chem., 32,* 1061 (1940).
[4] D. Cannegieter, *Verfkroniek, 19,* 126 (November 1946).

From these data it appears that while the values of k differ markedly for the different drying oils, the heats of polymerization do not vary a great deal. This might point to the same mechanism of basic polymerization, although oils with conjugated systems have a smaller heat of reaction than those consisting of nonconjugated triglycerides.

TABLE XVII-1

Reaction Constants of Heat-Polymerizing Drying Oils[1]

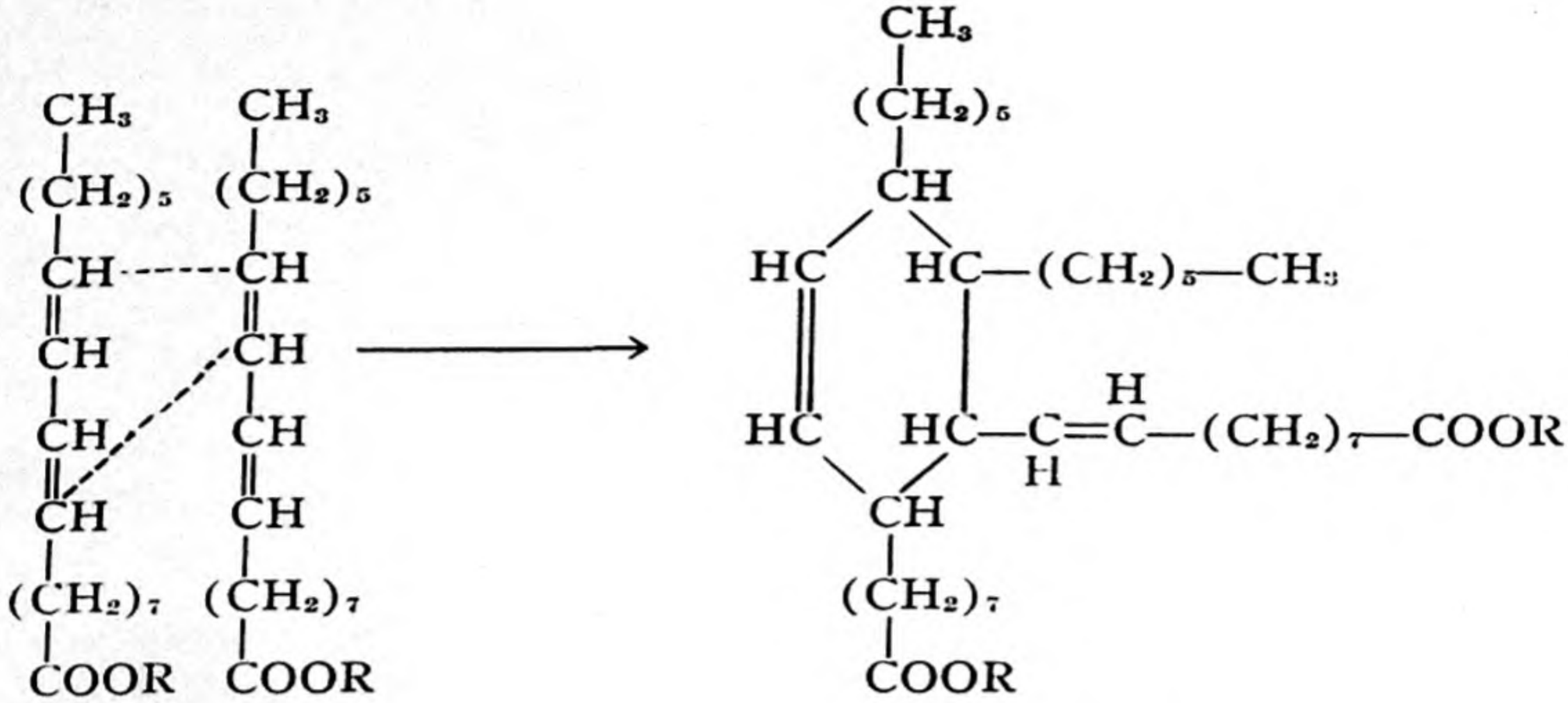
Oil	$k \times 10^{-3}$	Q/R, cal.	t (°C.)
Linseed	4.2	6400	300
Linseed	0.7	6400	250
Tung	55	4600	300
Dehydrated castor	8.8	6300	300
Oiticica	43	4900	250

The polymerization of linseed oil may be speeded up markedly by the influence of sulfur dioxide, with a resulting increase in the constant k. The magnitude of the increase depends on the gas concentration, from 4000 without gas up to 35,000 at the highest effective saturating gas concentration. Sulfur dioxide has no effect upon the rate of polymerization of oiticica oil. Consequently it appears that the gas catalyzes isomerization, the shifting of the double bonds into a conjugated position, but it does not influence the actual polymerization reaction.

Important information about the mechanism of thermal polymerization of drying oils has been obtained by the study of thermal polymerization of the methyl esters of the drying oils, the polymers of which may be separated by molecular distillation. The mechanism of polymerization appears to be the same as with the much less volatile glyceryl esters, since upon saponification both types of polymerized esters yield the same products. During the polymerization predominantly dimers are formed, with only small quantities of trimers. No higher polymers were found to be present.

Although the exact structure of the polymeric triglycerides is not known, it appears from extensive physical measurements that linkages formed during the polymerization are carbon-to-carbon bonds by primary valencies, indicating a Diels-Alder type of condensation.

The dimer is a six-membered ring system with an unsaturated side chain. As an example, dimerization of a 9-11 linoleate will proceed as follows:



This dimer may condense with an additional monomer molecule at either double bond, forming a trimer. The chance of additional condensations with other molecules is remote, and any further reaction must be regarded as intramolecular, increasing the rigidity of the complex without further increase in molecular size.

Heat-polymerized oils are used in preference to raw oils for printing ink vehicles. The polymerization, however, is never carried out to the gelation point, since the gels are generally insoluble and incompatible with the other printing ink vehicle components, although in special cases colloidally dispersed gels are sometimes used.

The formation of a stable film of a cross-linked polymer is desirable only in the final stage of oxidative drying of the ink film.

B. OXIDATIVE DRYING OF LINSEED OIL FILMS

The initial stage of an ink film printed on paper is usually a penetration of part of the vehicle into the stock. In inks based on drying oils, however, a complex series of reactions is then set in motion, resulting ultimately in the formation of the solid film.

In the process of heat polymerization the most important indication of the progress of the reaction is the viscosity of the vehicle, which increases rapidly with time after the induction period. A similar

effect occurs in a thin film of drying oil exposed to the air at room temperature. Banks and Upton[5] studied the behavior of the drying film in a simple system. Unpigmented films of bodied linseed oil were deposited in a uniform film thickness of 8.6 microns on glass. The glass plate was held at a predetermined angle, and a steel ball was allowed to roll along the surface. The time required for the ball to

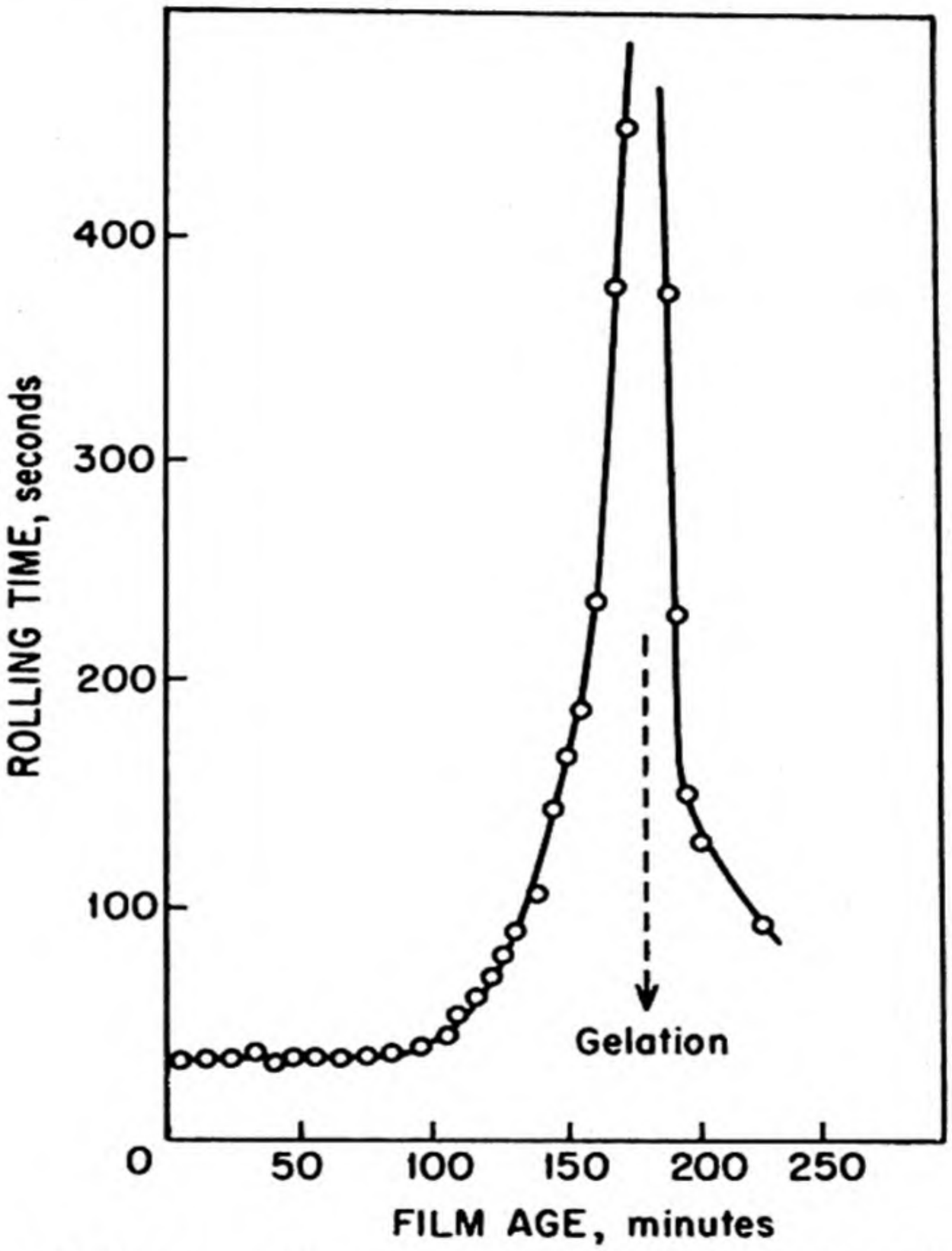


Figure XVII-1. Change of rolling time with film age.

traverse a given distance is an indication of the viscosity of the film, as was shown by a series of calibration tests with liquids of known viscosities.

Figure XVII–1 shows rolling times of the steel ball plotted against the age of the film for a heat-bodied linseed oil of a viscosity of 61 poises at 20°C. containing 0.05 per cent of cobalt calculated as metal. All experiments were carried out at a temperature of 20°C. ± 0.5. The curve, characteristic of all varnishes examined containing cobalt

[5] W. H. Banks and P. B. G. Upton, *J.O.C.C.A.*, *33* (363), 397 (1950).

driers, shows that up to approximately ninety minutes there is no appreciable change in rolling time of the ball. The film viscosity, therefore, remains constant. Beyond this induction period, however, the rolling times rapidly increase, reach a sharp maximum, and decrease thereafter. Inspection showed that when the decrease of the rolling time sets in the film has gelled. Diminishing rolling times, therefore, are due to the hardening of the gel. The sharpness of the point of gelation is most pronounced and was observed in all tests.

Experiments with varnishes containing lead and manganese driers show a similar result. The induction period for lead-manganese driers is somewhat shorter than for cobalt when expressed in fractions of the total drying time. Varnishes containing lead and manganese driers show marked changes in their drying properties with age. The data indicate a rapid initial drier deterioration followed by an increase

TABLE XVII–2

Rolling Times for Films of Different Ages[5]

Film age, min.	Mol. wt.	Rolling ball times, sec.	Approx. viscosity, poises at 20°C.
0	1735	30	50
28	1864	35	66
58	1902	35	66
115	2063	60	110
147	2317	150	700
172	3109 ?	430	—

in drying properties. These observations may be explained by the formation of insoluble lead salts. This view is supported by the well-known effect of a change in the relative concentration of lead and manganese in the drying liquid.

In addition to rolling times, Banks and Upton determined the change in average molecular weight of the film by the cryoscopic method, using cyclohexane as a solvent. Table XVII–2 indicates the molecular weights and rolling times for a bodied linseed oil containing 0.05 per cent cobalt.

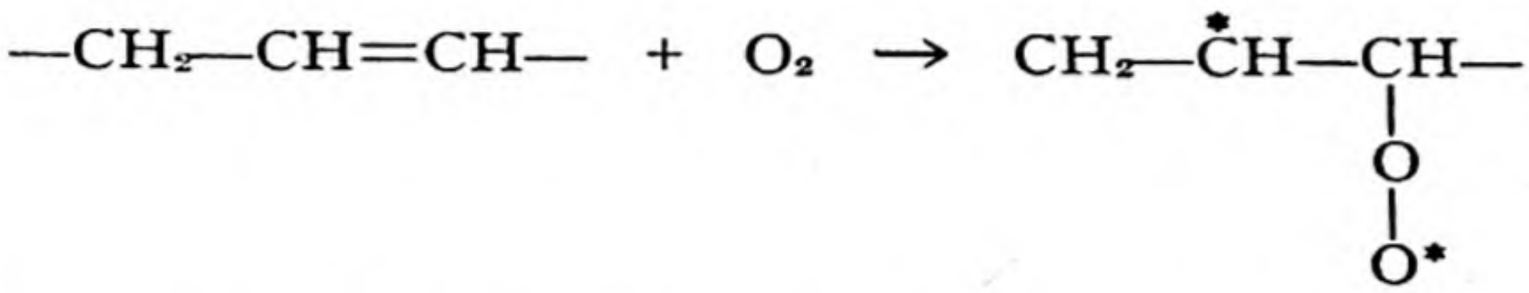
The molecular weight of the monomeric triglycerides is just below 900. The initial molecular weight of 1735 indicates the effect of the previous thermal polymerization of the oil.

A film aging of 147 minutes resulted in a completely soluble film

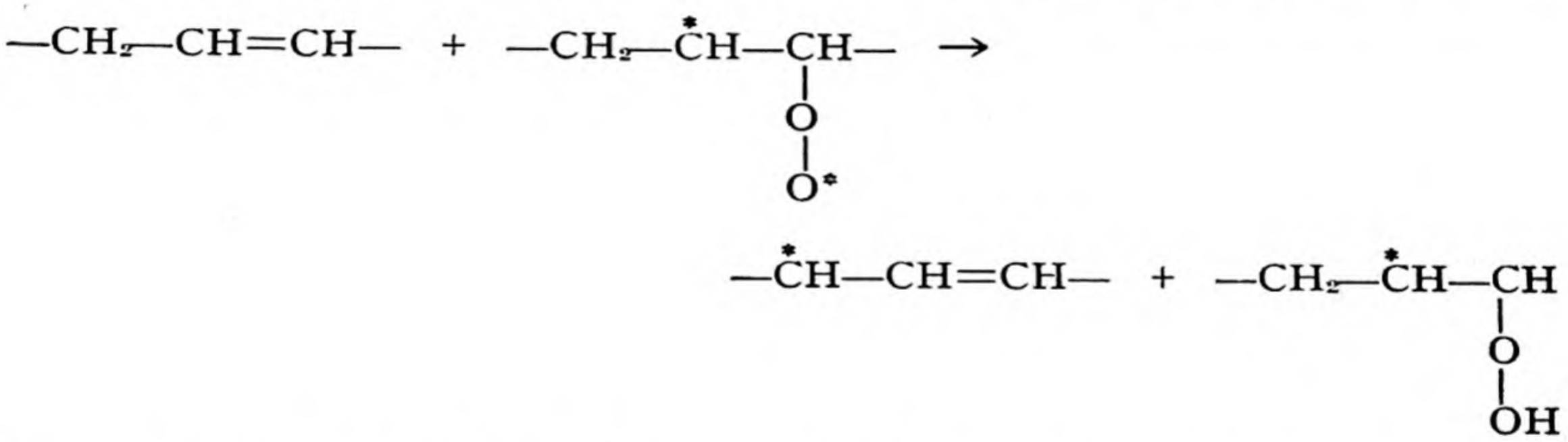
which remained clear. After longer aging time the film is not completely soluble in the solvent, and the molecular weight of 3109, found after 172 minutes aging, is not completely reliable. Thus, it appears that the average molecular weight corresponds to about a trimer at the gelation point.

The actual mechanism of oxidative polymerization appears to be of an even more complex nature than the thermal polymerization of drying oils.

There is evidence that the oxygen adds to the double bond to form a biradical:



This combines with another unsaturated group to yield two radicals:



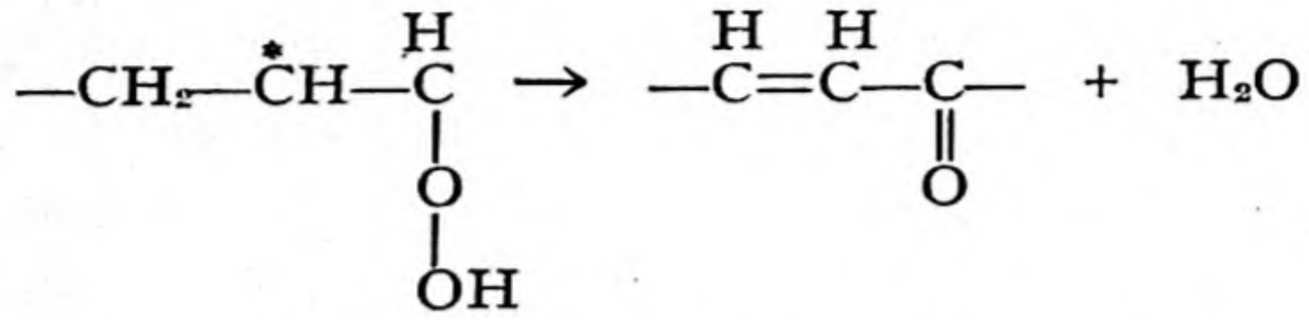
Thus, alpha methylenic hydroperoxides are formed, according to Farmer and Sutton,[6] who proved this hypothesis by the actual isolation of an oleate hydroperoxide from partly oxidized oleic esters.

In unconjugated systems the conjugation increased with the peroxide content. It was found[7] that by far the greater part of the peroxides formed by oxidation of unconjugated drying oils are conjugated. The peroxides formed in conjugated systems are usually conjugated, although some reduction in conjugation may occur upon oxidation.

The formation of peroxides is quickly followed by their decom-

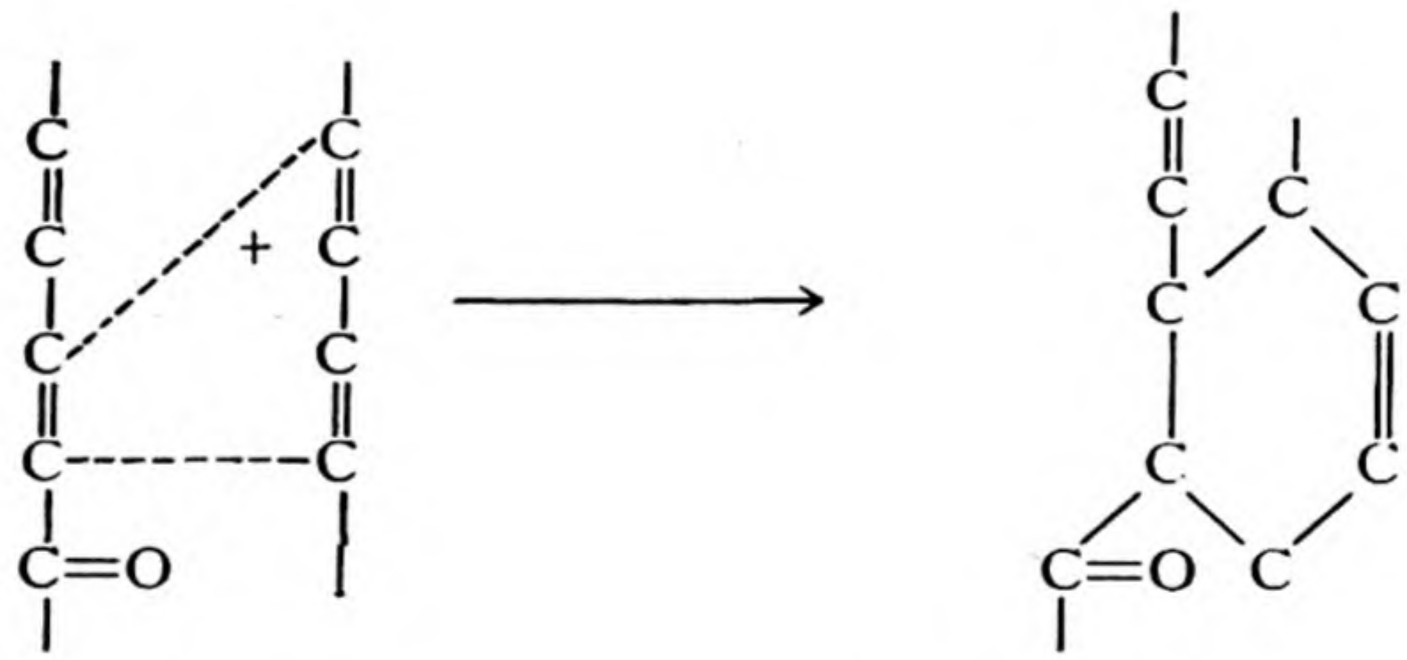
[6] E. H. Farmer and D. E. Sutton, *J. Chem. Soc.*, 119 (1943).
[7] W. O. Lundberg and J. R. Chipault, *J. Am. Chem. Soc.*, *64*, 833 (1947).

position, generally believed to be a dehydration. Schematically the following reaction takes place:

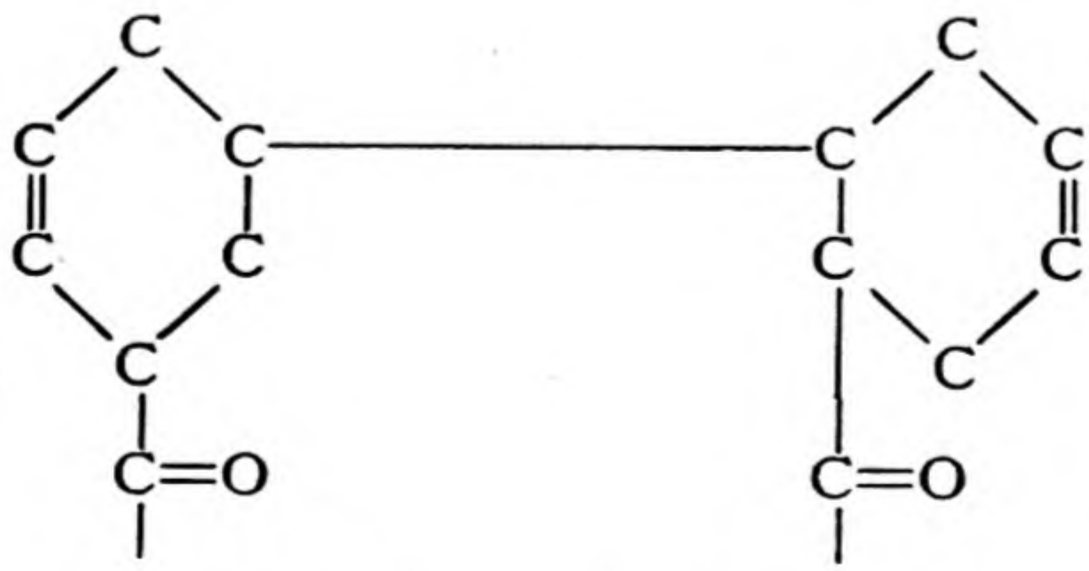


This is in accord with the general observation that water is evolved in the drying of oil films, amounting to 1–2 moles per mole of drying oil ester. Dehydration sets in only after a considerable quantity of oxygen has been taken up by the film.

The final stage of polymerization is, as with thermal polymerization, a Diels-Alder reaction, resulting in the formation of a six-membered ring:



The latter may in turn add on an additional molecule to form the following compound:



The chance of further condensation with other molecules now has become remote and, as in thermal polymerization, additional reactions will occur within the large complex itself with its numerous reactive

groups, leading to an increase in rigidity without increase in molecular size.

From the previous considerations it appears that the molecular weight of the polymer at the moment of gelation is rather low. Banks and Upton[8] concluded that this behavior is characteristic of three-dimensional condensation polymerization, in accordance with the theories of polymerization initiated by Carothers and developed by Flory and others.[9] According to these views a polyfunctional reactive molecule can form an infinite network structure resulting in gelation when the polymerization has proceeded to a certain extent, depending inversely on the functionality of the reacting units. Thus, for molecules with a large number of reactive groups gelation will set in at a low average molecular weight, while for molecules with few reactive groups a high extent of polymerization is required for gelation.

According to Flory, when M_n is the number-average molecular weight and M_0 that for the monomeric unit of functionality f, then if p is the extent of the reaction,

$$\frac{M_n}{M_0} = \frac{1}{1 - {}^1/_2 fp} \tag{45}$$

Gel formation sets in if the critical value of p is

$$p_{\text{gel}} = \frac{1}{f-1} \tag{46}$$

Banks and Upton calculated that the functionality of the molecules as a result of oxygen activation is not over 3, to account for the molecular weights found near the gelation points. The presence of three reactive groups in the fatty acid esters would therefore explain their behavior in the air drying film. This is a very likely occurrence, in view of the structure of the triglyceryl esters of the unsaturated fatty acids.

C. GEL STAGE OF THE DRYING OIL FILM

From the investigations of Bowles[10] a number of factors have become known which influence the characteristics of the gel stage of

[8] W. H. Banks and B. P. C. Upton, *J. O. C. C. A.*, *33*, (363), 397 (1950).
[9] W. H. Carothers, *J. Am. Chem. Soc.*, *51*, 2548 (1929). P. J. Flory, *J. Am. Chem. Soc.*, *61*, 3334 (1939); *62*, 1057, 2255 (1940); *63*, 3083 (1941); *64*, 2205 (1942). R. H. Kienle, *Ind. Eng. Chem.*, *22*, 590 (1930); *J. Soc. Chem. Ind.*, *55*, 229 (1936); *Trans. Faraday Soc.*, *31*, 48 (1935).
[10] R. F. Bowles, *J.O.C.C.A.*, *24*, 29 (1941).

a drying oil. A drying oil film of a known thickness was deposited on a disk. An ordinary steel record needle was slowly moved across the surface. By studying the track of the needle it was observed that initially the needle is drawn through a thin liquid, as seen from the inward flow of liquid from both sides of the track. At a later stage the liquid becomes more viscous, and finally a rather sudden gelation occurs, as may be observed from the track which appeared to be cut through solid material. By revolving the disk at a predetermined slow speed it is possible to estimate the exact period of time required for gelation to set in. Bowles observed that the gelation point is the only well-defined point in the process of air oxidation of a drying oil. This is an important finding, since it not only permits a more exact study of the transformation of the liquid into a gel, but also the gelation point is doubtless intimately connected with the point at which an ink may be considered sufficiently set for much of the mechanical handling required in the printing process. Bowles experiments may be summarized in a series of conclusions, which are as follows:

(1) The film thickness has no influence on the gelation time for films of a thickness less than 20 microns. In thicker films skin formation hinders the setting. This effect is nonexistent in printing ink films which seldom are thicker than 5 microns.

(2) The gel formation itself is hardly affected by moisture in the air or by emulsified water.

(3) Aging of the oil does not influence the setting time of the film.

(4) The temperature coefficient of the setting time is about 2 per 10°C. in the range of 0–70°C., and from then on about 1.5. This relationship is modified, however, in the presence of catalysts.

(5) The gelation time decreases with increased oil viscosity. For linseed oil the limit is reached at 150 poises at 25°C.

(6) The gelation time is proportional to the square root of the cobalt concentration for cobalt linoleate. With naphthenates and resinates similar relations were found, with slight deviations due to interference of the acid radical.

(7) The gelation time is independent of the acidity of the oil for oils of an acid number of over 7.

(8) The gelation time for a second film superimposed on the first film varies with the state of the first film. It is accelerated with newly gelled films, but is inhibited with films more than two days old.

(9) The influence of light on the gelation time is small, but a measurable decrease of the gelation time is observed.

(10) Sulfur dioxide speeds the polymerization but increases the gelation time.

These results are typical for nonpigmented films. The presence of pigments, however, may drastically modify the relationships indicated.

D. DRYING OF INK FILMS

1. Evaluation of Drying Time

Although inks may set in a relatively short period of time, the actual hardening of the film may take much longer. In order to study the process of ink drying on paper successfully, a reliable method is needed to determine the drying time of printing inks on any given paper stock. The "manual rub test," which is carried out by rubbing the finger repeatedly under pressure from the printed area onto the adjacent unprinted area indicates that a film is dry when the ink is not rubbed off. Yet since the method is not reproducible and therefore unreliable, it does not yield a permanent record of any significance. A mechanical method for the determination of drying time is required for a more reliable study of ink drying.

Although many investigators have experimented with a number of mechanical drying time recorders, the more successful have arrived at the same basic testing principle by determining the period of time required before an ink will cease to transfer to a covering sheet under pressure. More specifically, a measurement is made of the time required for artificially induced offset to cease. Many instruments have been developed which employ this principle. Generally a stylus or a geared wheel moves slowly under a predetermined pressure on a cover sheet placed on top of the drying print. The end of the offset trail indicates that the film has dried under the conditions of the experiment. Some instruments use a spiral stylus motion along a flat surface, or roll a geared wheel along flat strips of paper. A particularly concise form, known as the Ink Dryograph,[11] uses a helical stylus motion on a cylindrical surface to which strips of paper printed with the drying ink film are attached. There are indications, however, that the "offset" principle for measuring drying times does not coincide fully with the printer's requirements for a "dry" print, to be ready for the subsequent operation. Possibly a periodic rubbing of the film with a plastic tip under a constant pressure will allow more practically useful conclusions.

[11] E. Carman, *Am. Ink Maker*, *27*, No. 4, 30 (1949).

2. Mechanism of Drier Action

The mechanism of drier action is little understood. Drier metals usually possess various stages of valency, and their action has been attributed to their ability to take up oxygen and to act as an oxygen carrier in the process of peroxide formation, returning thereby to the lower stage of oxidation. However, the mere fact that a metal is able to exist in various stages of oxidation is not sufficient for it to be a drier.

It has been established that driers, in order to be active, have to be present in true solution. Colloidally dispersed metals were found inactive as driers. The metallic salts generally used as soluble driers are oleates, linoleates, resinates, naphthenates, and ethyl hexoates. Less significant are linoresinates (tall oil derivatives), soyates (soybean fatty acid salts), borates, and acetates. The metals commercially used in driers are cobalt, manganese, and lead. The activity of iron is too low at room temperatures for practical applications. Cerium salts, though excellent driers, are not commercially used for economic reasons. The drier action of other metals is of a doubtful nature.

The action of cobalt salts as driers differs from the action of manganese and lead salts. Cobalt, though a powerful drier, tends to catalyze the surface oxidation without promoting the polymerization, which leads to gel formation and hardening of the film. Lead and manganese, on the other hand, do not promote a rapid surface oxidation, but cause a general hardening throughout the entire film. Lead and manganese driers are seldom used separately, but when used in combination, they appear to have a beneficial effect on film drying.

Cobalt is required for poorly drying inks. In dry multicolor printing, where it is essential to prevent a too rapid hardening of the surface of the film, which would be inimical to a proper trapping, cobalt driers are avoided and a lead-manganese drier is preferred. In other cases a combination of all these metallic driers is often employed to promote a surface drying as well as a general film hardening.

3. Factors Affecting Ink Drying

Of the numerous investigations reported on ink drying few have been directed on a scientific basis. In most of the older investigations the various factors influencing the drying of inks generally have not

been separated sufficiently to allow definite conclusions. Valuable studies have been made by Reed *et al.*[12] and by Banks and Penney.[13]

From these and other recent investigations the effect of external and internal factors upon the drying of ink films based on linseed oil has become better known. Some factors may be considered separately, but there is a marked interrelationship between the many factors involved. Among the ink constituents, beside the drying oil, the pigments and the drier are the most important factors influencing the drying rate of the ink film. Film thickness and availability of oxygen affect the drying rate; the presence of antiskinning agents may also have a considerable effect. Of the external factors the humidity and the temperature have a profound influence, and the paper stock used is of significance. In the offset process the acidity of the fountain may influence the drying speed of the inks. Finally, the storage period of the ink may have a pronounced influence upon its drying time.

4. The Pigment

Pigments may greatly vary the drying time of a drying oil film. Three groups may be differentiated; namely, pigments which promote drying, those which retard drying, and those which do not affect the drying of inks.

Pigments which promote drying, often known as "natural driers," are iron blues, chrome yellows, and chrome greens. A typical promoter of film drying under all conditions is iron blue. The exact mechanism of the drying-promoting action is not known, but it does not seem unlikely that the presence of complex iron salts has a catalytic action on the oxidative phase of oil drying in a way somewhat similar to the action of the conventional driers. Chrome pigments may have a different type of action, since they are not effective with cobalt driers and act only in the presence of manganese.

The class of drying retarders is represented prominently by carbon black. In addition, phosphotungstated colors, such as permanent violet, are notorious retarders of drying action. The mechanism through which retardation of drying is achieved is of a complex nature. In carbon black, drier adsorption, no doubt, plays an important part.

[12] R. F. Reed, L. E. Caldwell, and R. L. Benemelis, *Research Bull.* No. 13, Lith. Tech. Foundation, New York, 1944.

[13] W. H. Banks and J. R. Penney, *Tech Paper* No. 8, PATRA, London, 1941.

Most of the remaining pigments are inert, indicating that they do not have a pronounced positive or negative influence upon the drying time of the film. From the fact that so many pigments are inert it appears that even at a high pigment loading purely steric factors, such as obstruction of oxygen diffusion or interference with orientation and arrangement of molecules in the polymerization process, do not play an important part.

The influence of the pigment concentration upon the drying time is entirely in accordance with their qualitative effect. For this reason drying retarders, such as carbon blacks, will increase the film drying retardation in higher concentrations, while drying promoters will dry better when more of the pigment is incorporated in the film. Finally, inert pigments do not greatly affect the film drying time, regardless of their concentration.

5. Atmospheric Humidity

An important factor influencing ink drying is the atmospheric humidity. The effect of the humidity is not the same for all pigments. Thus, the drying of lithol rubine B and of chrome yellow is hardly affected by a relative humidity up to 95 per cent. On the other hand, milori blue, methyl violet, and carbon black require more and more drier to maintain the same rate of drying as the relative humidity increases. For a carbon black ink at least twice as much drier was required at 80 per cent humidity than at 30 per cent to dry in the same period of time, and at a relative humidity of 95 per cent more than three times as much drier was required. Manganese and lead driers are not satisfactory for carbon black inks at humidities above 70 per cent. At higher humidities cobalt driers are required.

Other pigments generally require an increase in drier concentration to maintain their rate of drying at higher humidities, although the influence of the air humidity is not as pronounced as with carbon blacks.

6. Temperature

Ink films dry faster at higher temperatures. A rise of about 10°C. in temperature generally reduces the drying time by a factor of 2. The temperature coefficient of the rate of drying therefore does not differ much from the temperature coefficient of the rate of chemical reactions in general, which is of the same order of magnitude.

7. Film Thickness and Oxygen Availability

The availability of oxygen has a marked influence upon the drying time of ink films. Prints of a film thickness of 3 microns did not require a longer drying time than inks of about twice this film thickness when allowed to dry separately. When placed between unprinted sheets separated by glass plates the drying time was nearly doubled. This indicates that commercial prints dried on a pile, the compression of which reduces the amount of oxygen available, will require a longer drying time than when dried separately. The effect is more pronounced for heavier ink films.

Ink films are seldom thicker than 5 microns. The formation of a surface skin preventing adequate oxidation of the covered part of the film therefore does not play a part in ink films.

8. The Drier Concentration

The effect of the drier concentration upon the rate of drying of inks is complex. A number of pigments tend to adsorb the metals from the ink, inactivating the drier action. For example, it was found that carbon blacks may adsorb as much as 20 per cent of their weight of a cobalt drier containing 3 per cent of metal. In inks containing 25 per cent of carbon black the pigment, therefore, could eliminate as much as 5 per cent of drier from the vehicle. Under these conditions at least 8–9 per cent of drier is required for an effective drying.

In general, the drying time of inks decreases with increasing drier concentration. The increase becomes gradually less pronounced, until finally a saturation point is reached. Higher concentrations of drier not only fail to increase the rate of drying of the ink film, but may also actually increase the drying time, as a result of the introduction of the inert materials present in the driers. The saturation point depends on the type of pigment used, the pigment concentration, and the relative humidity. In general, the saturation concentration for the group of drying retarding pigments is rather high. Experiments carried out at 29°C. showed that for a commercial offset black containing 25 per cent of carbon black the rate of drying increased rapidly with the concentration of a cobalt naphthenate drier containing 3 per cent of cobalt up to a concentration of about 10 per cent. Little advantage was gained by using additional drier at a relative humidity of 44 per cent or less. At higher humidities, however, there was a

decided advantage in adding more drier. Thus, at 81 per cent humidity a concentration of 16 per cent of drier showed an improved rate of drying, while at 95 per cent relative humidity the optimum was reached at about 20 per cent of drier. Similar results were noticed with other drying retarding pigments.

An optimum drier concentration, generally not very sensitive to changes in the relative humidity, is also observed for inert pigments and for pigments promoting the drying. The actual drier percentage of the maximum depends on the individual pigment. With lithol rubine B inks, for instance, a maximum drier effect was found at a concentration of 3 per cent of a lead manganese drier containing 13.1 per cent of lead and 2.6 per cent manganese. The use of more than 3 per cent of this drier was not an advantage at any relative humidity. For chrome yellow the optimum was set at about 2 per cent of drier. For a tungstated violet toner the rate of drying increased markedly with the concentration of a cobalt naphthenate drier containing 3 per cent cobalt, up to 6 per cent of the drier. More than the indicated quantities did not improve drier qualities at relative humidities below 80 per cent. At higher humidities, however, a marked improvement in drying was seen upon increasing the drier concentration up to about 12 per cent of drier. From these facts it appears that each pigment is essentially a different problem, and the optimum drier concentration has to be established experimentally for different relative humidities.[14]

E. INFLUENCE OF PAPER

The stock upon which the ink has been printed affects the drying speed in more than one way. As previously discussed, the surface permeability has an important effect on the ink setting, being connected with vehicle absorption. If the vehicle penetrates too fast in the paper or if the rate of drying is too slow, not enough binder remains in the film and the pigment is insufficiently protected and does not adhere properly to the paper. This leads to chalking, characterized by a loosely held film which crumbles and detaches from the paper with light mechanical handling. To obtain a properly protected, well-adhering film a definite ratio has to exist between the rate of drying and the rate of vehicle penetration into the paper stock.

[14] R. F. Reed, L. E. Caldwell, and R. L. Benemelis, *Research Bull.* No. 13, Lith. Tech. Foundation, New York, 1944.

Drying is most rapid on coated stocks. No significant differences are observed in the drying rate of a given ink on various noncoated stocks at lower humidities. At higher humidities, however, drying is retarded more on supercalendered paper than on bond stock. Offset papers act similarly to supercalendered papers.

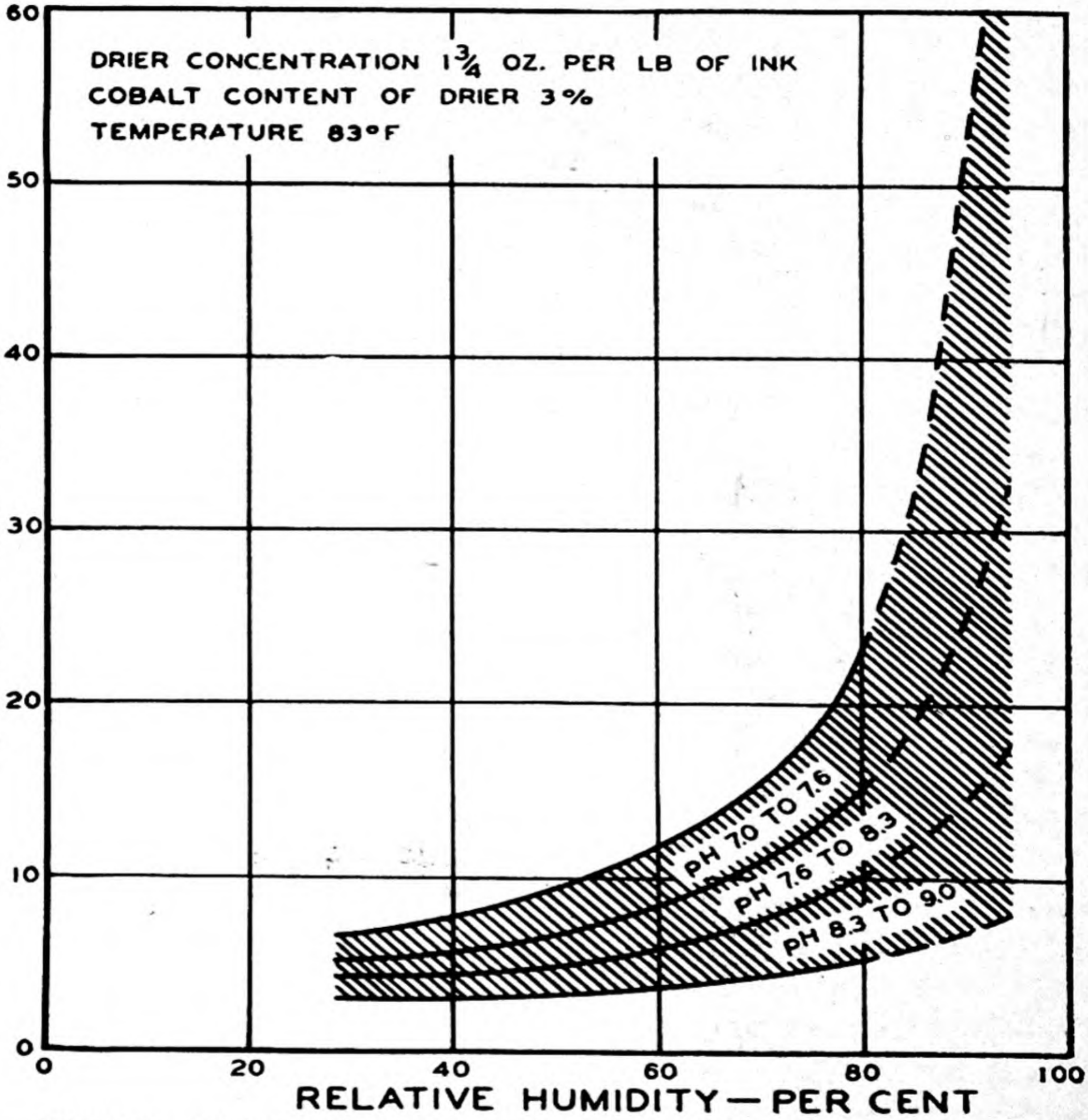


Figure XVII-2. Relation between drying time and relative humidity for an offset black ink on coated stock of different coating acidities.[12]

In coated papers the alkalinity of the paper plays an important part. Figure XVII–2 shows the influence of the pH of the paper surface upon the drying time of a black offset ink at different relative humidities indicating the advantage of alkaline reacting paper.[14]

There is no doubt that acidity in papers causes serious drying troubles. The reason for this phenomenon is that the reaction of acid materials in the paper with the drier metal results in the formation of oil-insoluble reaction products.

Coupe and Banks[15] investigated the adsorption of cobalt naphthenate from linseed oil by cellulose fibers by means of chromatographic analysis. It was found that pure cellulose fibers have very little tendency to adsorb the cobalt salt. Acidified fibers, however, showed a markedly increased tendency to cobalt adsorption. The experiments indicate that the retardation of drying by paper of a low pH may be the result of elimination of cobalt drier from the ink by adsorption by the paper fibers. The effect of paper acidity is most pronounced for offset papers in the presence of moisture, because offset ink films always contain appreciable quantities of water emulsified in the ink. For typography, in the absence of moisture, the effect is less marked.

F. INFLUENCE OF ACIDITY OF OFFSET FOUNTAIN SOLUTION

An effect characteristic of offset inks is the influence of the acidity of the fountain solution. Under normal printing conditions the fountain solution is slowly emulsified into the ink, until 5–15 per cent aqueous liquid is incorporated. Water-in-oil types of emulsion inks do not show a great deal of drying retardation when pure water is emulsified, provided excess moisture is allowed to escape from the film. A serious retardation effect may result, however, from the emulsification of fountain solutions of greater acidity than the usual pH of 3.8. Table XVII–3 shows the drying time for a commercial offset black, depending upon the fountain acidity.[14] The effect, no doubt, is caused by a chemical reaction between the drier and the

TABLE XVII–3

Drying Time and Fountain Acidity for Offset Black[14]

Paper	Drying time, hours for solutions of pH:				
	7.0	3.8	3.6	3.0	2.0
Offset, felt side	12	16	17	22.5	70
Bond, felt side	15	21	22	32	84

[15] R. R. Coupe and W. H. Banks, *Research, 3,* 528 (1950).

acid present in the water, resulting in the formation of oil-insoluble cobalt salts.

G. EFFECT OF ANTISKINNING AGENTS

Occasionally antiskinning agents are used to prevent skin formation on the surface of the ink in the can. These agents are usually of a phenolic or aromatic amine character. The antiskinning action is due to their antioxidant properties.

Antioxidants are inhibitors of the drying of oils in extremely small concentrations. They act by preventing the formation of the peroxides, essential chemical intermediates in the oxidative drying of oils. Consequently, the natural induction period, caused by the presence of naturally occurring inhibitors, is increased by artificial inhibitors. The increase is usually proportional to the concentration of the antioxidant up to a certain saturation limit, beyond which the activity may even decrease. The effect of antioxidants is less pronounced at higher temperatures. At the end of the increased induction period the rate of oxidation of the oil is generally not retarded. Driers, which reduce the inhibition period and accelerate the oxidation therefore do not merely counteract antioxidants, but act on a different phase of the drying process.

Hydroquinone, a classical example of an antioxidant, is a very effective material to prevent oxidation in low concentrations, but it is seldom used in inks. Phenols, such as alpha and beta naphthol and phenol-modified indene, are practically used to prevent skinning of inks in cans by inhibiting the oxidation. Great care should be taken in using antioxidants, since the indiscriminate addition of these powerful agents may lead to an undue retardation of the drying of the ink. The use of volatile antioxidants has considerably less risk, since these materials, though inhibiting drying in the ink can, rapidly disappear from the printed film by evaporation.

H. LOSS OF DRYING UPON AGING

It is a common occurrence that certain inks, which dry satisfactorily after being made, lose their drying ability progressively with age. Pronounced losses of drying ability are usually found in carbon blacks, titanium dioxide, most lake pigments, and to some extent, phthalocyanine pigments. Analysis shows that dissolved drier

metal is no longer present and has been removed from the vehicle by adsorption or by a chemical reaction.

Zettlemoyer *et al.*[16] showed that feeder driers, acting on the principle that a sparingly soluble drier dissolves in the vehicle to replace the soluble metal taken up by the pigment, maintain a fairly constant level of drier metal concentration in the vehicle for long periods of time.

Cobalt borate is a satisfactory feeder drier. It goes into solution by means of an exchange reaction with the fatty acids present in the vehicle. As an example, a drying time level for a yellow lake ink

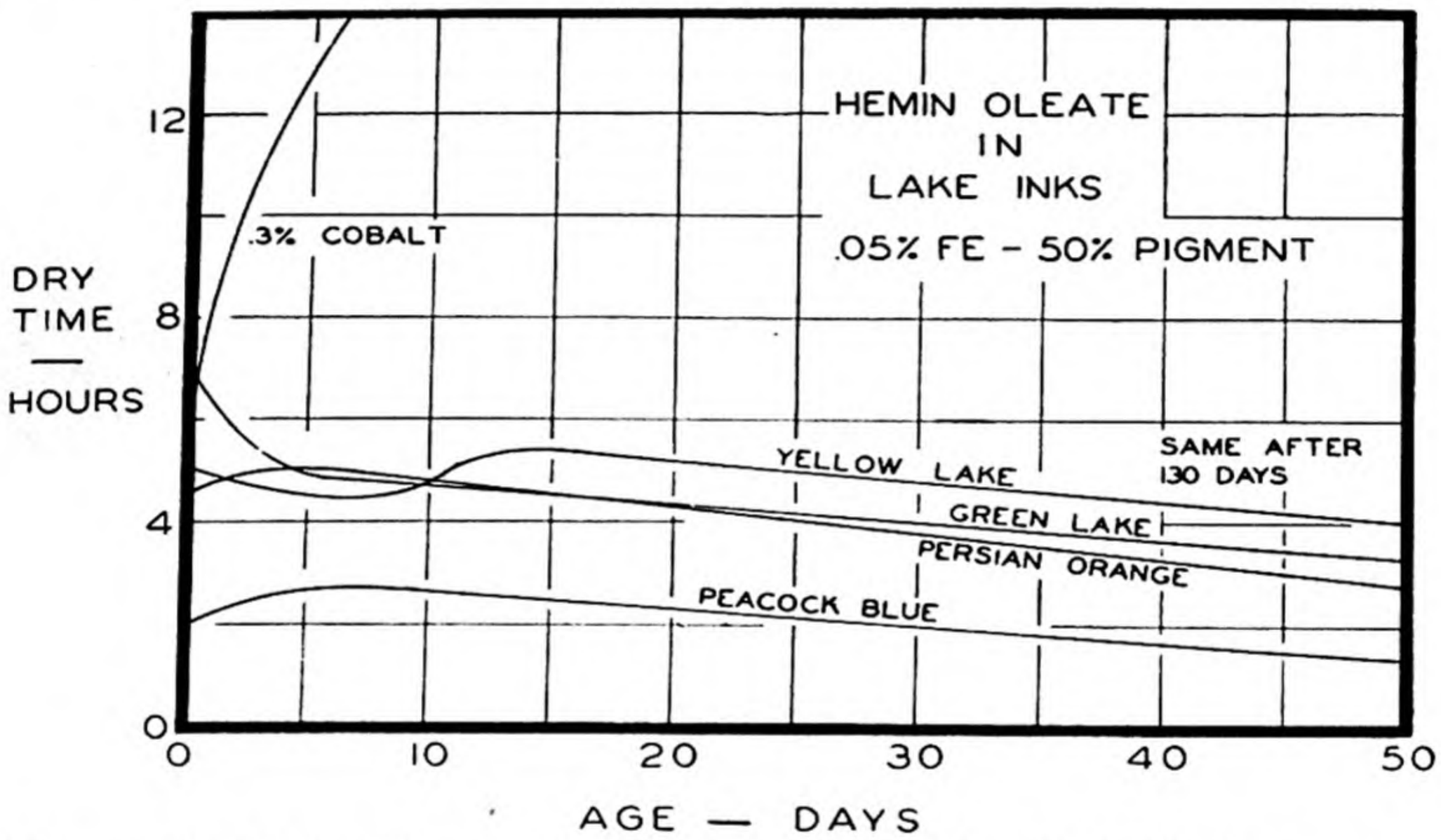


Figure XVII-3. Hemin oleate compared with cobalt linoleate as a drier in lake inks.[17] Percentages of metal are based on the vehicle.

could be maintained at eight to ten hours for only two days with the soluble drier cobalt linolate. With the feeder drier cobalt borate, this drying time was maintained for 100 days, and even after six months there was very little loss in the rate of drying. The best results were obtained with a combination of a feeder drier and small amounts of a soluble drier and indicate that in this way a practically constant drying time level may be obtained.

Zettlemoyer and Nace[17] showed that the porphyrin-iron complex

[16] A. C. Zettlemoyer, G. W. Lower, and E. Gamble, *Ind. Eng. Chem., 41,* 1501 (1949).

[17] A. C. Zettlemoyer and D. M. Nace, *Ind. Eng. Chem., 42,* 491 (1950).

hemin, obtained from hemoglobin of the blood, is very effective in catalyzing the oxidation of the drying oils. Figure XVII–3 shows a comparison of cobalt linolate as a drier in lake inks with hemin oleate. It appears that the complex iron is not absorbed and does not enter into a reaction and actually improves its drier properties on aging, while the cobalt drier lost most of its drier activity in a short period of time.

The use of hemin derivatives as driers is not economically feasible, but other metallic complexes have similar properties. Thus, Zettlemoyer and Nace[17] found that complexes of manganese with ortho-phenanthroline are very effective driers which do not disappear from the vehicle upon aging of the ink. They found that it is not necessary to prepare the complexes directly since, upon addition of ortho-phenanthroline, they are formed in the inks containing driers as a soluble oleate.

Excellent results were also obtained with aromatic amines. Particularly successful was 2,4,6-tri(dimethylaminomethyl)phenol, a material known by its trade name DPM-30. Figure XVII–4 shows the influence of DPM-30 in different concentrations upon the drying time of a yellow lake after aging, indicating that relatively small quantities of DPM-30 will prevent loss of drying on aging.

DPM-30 is also effective in the recovery of drying properties of inks that have aged. Figure XVII–5 shows the results of the addition of 0.7 per cent of DPM-30 to a yellow lake containing 0.3 per cent cobalt, after the ink had been allowed to age for varying periods of time. The drying time drops immediately from a very high value to a usable range and stays there for some time.

DPM-30 has to be used with caution. An excess retards the drying action. DPM-30 added to inks which do not lose their drying properties with age may act as a drying inhibitor.

The retardation of drying upon aging of the ink may be caused by several processes. In inks containing nonreactive pigments, such as carbon blacks, the drier is effectively removed from the solution by adsorption, as discussed previously. In color lakes, however, a chemical reaction may be responsible for the elimination of the drier. In alumina hydrate, the base for most color lakes, the particles are surrounded by a film of acidic water, which effectively extracts the drier metal from the oil phase. In addition, the presence of strong oil-soluble organic sulfonic acids, introduced as surface-active agents

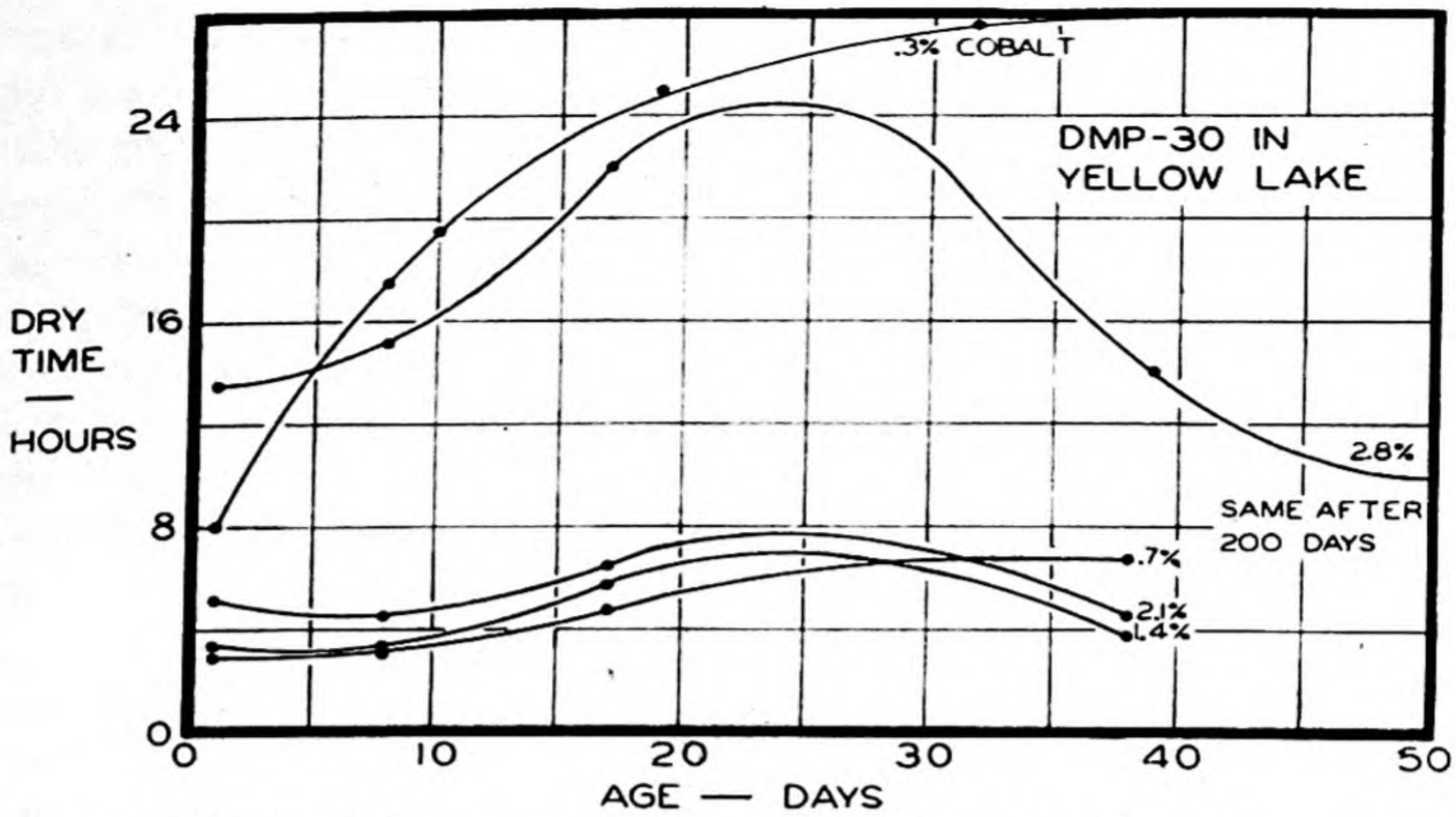


Figure XVII-4. Effect of various amounts of DMP-30 on the aging of yellow lake ink.[17] The percentages of DMP-30 are based on the ink.

or present from incompletely fixed dyes, will cause a reaction with the drier metal which results in the formation of oil-insoluble inactive compounds.

Prevention of loss of drying on aging may be accomplished by the gradual replacement of lost driers by a feeder drier or by a complexing agent which protects the drier metal from adsorption or from a chemical reaction without eliminating the drier activity.

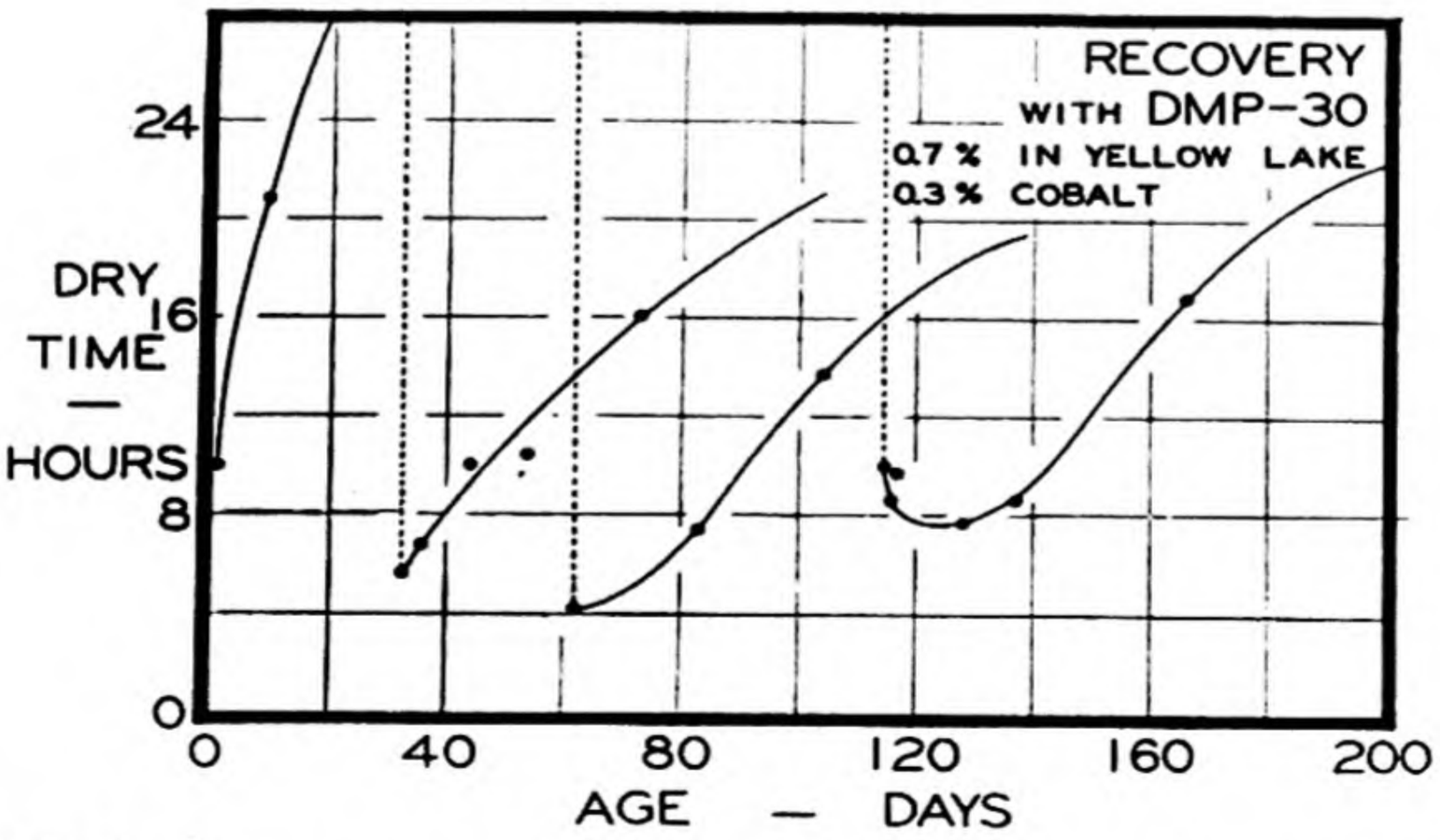


Figure XVII-5. Recovery of drying ability with DMP-30 in an aged yellow lake ink containing cobalt linoleate drier.[17]

Zettlemoyer and Nace[17] found that in the presence of alumina hydrate lakes all the DPM-30 added to the ink was taken up by the pigment, but the cobalt adsorption normally occurring was not reduced by the amine adsorption. Yet the drying time did not increase appreciably upon aging in the presence of the adsorbed DPM-30. Although it seems possible that the reduction in acidity of the pigment by the amine adsorption creates a more favorable condition for drying, the action of the amine in preventing drying loss on aging in alumina hydrate lakes is not yet fully understood.

One possible explanation is that, without amine, irreversible reactions occur in the pigment-oil interface between the drier metal and the acid present in the water film around the pigment particles. but that in the presence of the basic amines the drier is loosely bound. forming a kind of feeder drier complex.

I. CURING OF INK FILMS

Curing is the process of rendering a plastic material insoluble and infusible by heat, by chemical means, or by a combination of both processes simultaneously. Strictly, one should consider the oxidative polymerization of drying oil films as a form of curing. Actually, however, curing of ink films is understood to comprise all forms of polycondensation and polymerization except oxidative polymerization.

In the acid catalyzed reaction of formaldehyde and phenol a soluble and fusible low polymeric intermediate condensation product known as Novolak is formed. The Novolak is converted in a second step by reaction with materials providing methylenic links, such as hexamethylenetetramine, into the insoluble and infusible cross-linked polycondensate known as resinoid.

The process of conversion may be speeded up considerably by heat and by catalysts. Application of the material in a thin film contributes materially to a rapid conversion. Yet, a setting time of a few seconds, which may possibly be reached in extreme cases, is by far too slow to be used in high-speed printing.

One of the difficulties involved in applying polycondensation reactions to the drying of printing ink films is the induction period, which apparently prevents the curing from being carried out in a fraction of a second.

A number of reactions suitable for the curing of ink films have

been proposed in the literature. Partly polymerized phenol-formaldehydes, urea-formaldehydes, and melamine-formaldehydes have thermosetting properties and will form cross-linked insoluble and infusible films upon heating for a short period of time with the proper catalyst. Dihydric polyesters of unsaturated dicarboxylic acids, such as diethyleneglycol maleate, are capable of a rapid further polycondensation to solid films under the influence of heat. Other thermosetting binders proposed for inks are melamine-formaldehyde-glyceryl sulfide condensates capable of further polycondensation.

Films of thermally coagulable proteins, such as albumen, solidify rapidly upon application of heat.

Rapid curing as a result of the influence of ultraviolet light occurs in drying oils with conjugated double bonds to which 1–10 per cent of dicinnamal acetone has been added.[18]

Curing due to chemical action has been achieved by exposing prints to chemicals promoting a polycondensation reaction. The chemical may be present in the paper, or the print may be exposed to the chemical in a finely divided liquid or vapor form. Thus, prints made with inks consisting of conjugated drying oils solidify rapidly when exposed to vapor of tin tetrachloride. The accelerated drying action of sulfur dioxide and of ozone upon drying oils, though a form of curing, is actually a catalyzed oxidative polymerization.

None of the methods proposed for polymerization and polycondensation has achieved any commercial success. It does not seem likely at this time that the curing method of ink drying will achieve much prominence in high-speed printing in the near future. An important reason is the already indicated induction period inherent in curing. In addition, potential reactants for curing inks are highly reactive and often corrosive. Many are toxic and have an offensive odor. They are generally complex mixtures economically not competitive with the nonreactive low-priced heatset inks and do not require much less heat to dry by curing than heatset inks do to dry by solvent evaporation. The use of thermosetting inks, therefore, will most likely be restricted to specialty applications.

[18] P. Whyzmusis, U. S. Patent 2,406,878, Sept. 3, 1946.

CHAPTER XVIII

PROPERTIES OF LITHOGRAPHIC INKS

A. GENERAL REQUIREMENTS FOR LITHOGRAPHIC INKS

Lithographic inks do not differ basically from letterpress inks, but the former have to fulfill more rigid requirements than the latter.

The principal distinction between these types of ink is that lithographic inks are used in intimate contact with the acidic fountain solution. In addition, in offset lithography, inks are subjected to a double transfer, namely, from plate to blanket and again from blanket to paper. Each of the specific demands of the offset process imposes its own particular requirements upon the inks used in the process.

The rubber blanket requires the absence of all aromatic solvents. Lithographic heatset inks must be completely non-aromatic in composition.

The double ink transfer results in a thickness of the ink film deposited on paper of about 1–2 microns, approximately half the film thickness used in typography. In order to obtain a proper covering of the paper with such a thin film, lithographic inks are made of the highest color strength obtainable by using pigments with high tinctorial strength and by applying the highest pigment loading compatible with a proper ink flow. As a result offset inks are usually much more viscous than letterpress inks at comparable speeds.

The intimate contact with water or with aqueous solutions results in a complex set of requirements for a lithographic ink. It is perfectly obvious that the ink constituents, such as pigment, vehicle, and drier, must not dissolve or disperse in water, neither in mere contact nor when subjected to shear, since ink and water are continuously brought together under shear by the rapidly rotating plates and rollers.

Ink and water films in intimate contact under shear will always show a certain amount of emulsification. As long as the emulsion is of the water-in-oil type it will generally not prevent the proper functioning of the lithographic ink.

It has been shown[1] that as much as 30 per cent of water could be emulsified in an ink without harmful effects. Usually, however, more than 15 per cent of water may cause the formation of a "water-logged" ink. Such inks show poor rheological properties and especially a high yield value. The reason is that the presence of water in the ink will cause the pigment particles to adhere to each other by means of a film of water, resulting in the formation of particle structures showing high yield values.[2] Water-logged inks are buttery, pile up, and show a faulty transfer, causing a poor reproduction.

Other failures of the process of lithographic printing may also be connected with the ink. They are known as tinting and greasing.

B. TINTING OF LITHOGRAPHIC INKS

Tinting is said to occur when a light tint shows over the entire plate which transfers to the blanket and finally to the entire area of print. A tint may be easily wiped off, although usually it will reappear immediately. The easy removal without injury to the plate as well as its general appearance in all parts of the print is characteristic of a tint.

The actual cause of tinting is the formation of an oil-in-water type of ink emulsion. A microscopic examination of the tinting particles indicates that they are small ink droplets emulsified in the dampening solution. They may be formed from an originally existing water-in-oil type of ink emulsion by a process known as phase reversal, not uncommon in emulsions.

The most important cause of tinting is a low vehicle viscosity which greatly facilitates emulsification and phase reversal. Another contributing cause is the preferential wetting of the pigment by the water phase. For this reason water-attracting (hydrophilic) pigments will promote tinting. The presence of moisture on water-repellent pigments such as carbon black facilitates tinting. The use of pretreated pigments coated with a hydrophobic material acts to prevent tinting, provided, however, that no additional complication arises from the introduction of surface-active agents often employed in pretreating pigments.

The lack of wetting of the pigment particles by the vehicle may

[1] R. F. Reed, L. E. Caldwell, and R. L. Benemelis, *Research Bull.* No. 13, Lith. Tech. Foundation, New York, 1944.

[2] H. R. Kruyt and F. G. Van Selms, *Rec. trav. chim., 62,* 407, 415 (1943).

induce tinting, since the water will more easily contact the incompletely wetted than the thoroughly wetted particles. Therefore, aged inks, which are generally completely wetted, will show less tendency to tinting than freshly prepared inks. For the same reason vehicles with good wetting characteristics are more suitable to prevent tinting than vehicles with poor wetting qualities.

C. GREASING

Unlike tinting, greasing is not an overall effect on the lithographic plate, but is characterized by the formation of ink-receptive centers on water-receptive areas of the plate. Greasing cannot be removed without injury to the plate. According to Zettlemoyer[3] greasing is caused by a migration of surface-active agents from the ink to the nonwork area. On a zinc plate, for instance, the grained surface is coated with a zinc salt-gum complex formed during the desensitization process and maintained by the chemicals of the fountain solution. If a surface-active agent of the proper structure migrates from the ink, it may be adsorbed by the zinc salt coating with its polar group orientated toward the plate. The hydrophobic nonpolar part will then create an ink-receptive center in an ink-repellent area, resulting in greasing.

The surface-active agents responsible for greasing may be present in the vehicle, drier, pigment, or in any ink additive. They may even have been incorporated in the paper coating used in the printing and eventually find their way to the plate via the dampening solution.

A proper lithographic ink must be made up from ingredients which are water resistant. It must not show tinting or greasing. Its tinctorial strength must be higher than used in typographic inks.

According to a theory developed by Carman[4] a lithographic ink is prevented from properly functioning by a low viscosity, by pigment flocculation, and by greasing. It is stated that greasing is promoted by the use of hydrophobic pigments in conjunction with hydrophilic vehicles. At the present time, however, the experimental evidence presented in favor of this theory is scant.

D. SPOTTY INK DRYING

It is occasionally observed in lithographic printing with inks based on drying oils that at some period after the print has been made

[3] A. C. Zettlemoyer, *Am. Ink Maker, 27* (1), 27 (1949).
[4] E. Carman, *Am. Ink Maker, 28* (2), 25; (3), 36 (1950).

the film can be removed by manual rubbing, with the exception however, of a number of small patches and circular areas of properly dried film. These areas may be isolated, but they are frequently formed along the edges of other printed areas. This condition is known as spotty ink drying. R. R. Coupe[4] showed that this irregular drying of lithographic inks is not caused by inhomogeneities of the paper, as was frequently thought, in view of the fact that spotty drying could be produced in films deposited on nonabsorbent surfaces, such as glass and metal foils. It appeared that spotty drying is not directly related to a particular pigment or drier, but must be considered as a general phenomenon in oxidative drying. It is an intermediate stage in the drying process of films of drying oils, which apparently starts with the formation of small circular dry spots. These areas rapidly grow and finally cover the entire film. They are usually not observed under normal drying conditions, since this initial phase of drying may only last for a rather short period of time. Spotty drying becomes apparent and may cause difficulties only in poorly drying films. Since a low rate of drying is not uncommon in lithographic inks, as a result of the presence of dispersed acidic fountain solution in the ink, discussed in Chapter XVII, spotty ink drying, although not necessarily restricted to lithographic inks, is a typical defect encountered in lithography. It is easily remedied by increasing the rate of drying, which may be carried out by using additional drier, or by preventing loss of drying on aging, as indicated in Chapter XVII.

Coupe's investigations prove that the oxidative polymerization of films of drying oils does not occur homogeneously throughout the film, but is initiated by nuclei. The fact that the drying of a second film adjacent to or superimposed on the first film occurs predominantly in the adjacent or superimposed areas, emphasizes this conclusion.

It could not be deduced from these experiments whether the formation of hydroperoxides, or of free radicals, or the polymerization proper is initiated by nucleation. It is remarkable, however, that the study of a seemingly trivial phenomenon such as spotty drying of lithographic inks has furnished an important clue to the fundamentals of oxidative film drying.

[4] R. R. Coupe, *J.O.C.C.A.*, *35*, 118 (1952).

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